PRESENT TRENDS IN POLYMER DEGRADATION

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Polymer degradation reactions have aroused interest for as long as polymeric materials have been used commercially. Papers were published more than 100 years ago[1, 2] reporting extensive chemical investigations into the oxidative deterioration of rubber and gutta percha. However, the systematic study of polymer degradation reactions, which has continued to the present time, only started about 1930 with the birth of the modern synthetic plastics industry. At that time only a very limited number of synthetic materials were available and there was then, as now, a continuous demand to use them in an ever widening range of applications under more and more extreme conditions. The stabilization problems which arose had to be solved quickly and fundamental chemical investigations in a polymer chain environment were usually found to be difficult. For these reasons the main emphasis was on the stabilization of existing materials by the use of additives and this was usually achieved without any clear idea of the chemistry involved. The few papers which were published before 1945 were principally concerned with theoretical aspects such as the consequences of random and non-random cleavage of polymer molecules. By 1950 fundamental chemical work was being done, although for the same reasons as previously, it lagged far behind the rapid development of new materials which had begun to take place.

Real progress in inderstanding polymer degradation began to be made in the period 1950 to 1955. There are a number of reasons for this and it is of interest to review some of the more important in order to appreciate how the subject has developed to the present time and to see how it may be most profitably extended in the future.

Methods were being developed at the beginning of this period whereby the loss in weight and the rate of production of volatile material could be accurately followed. At the same time methods of molecular weight measurement, especially viscometry and osmometry, were being established so that the molecular weight changes which occurred in the residue during degradation could be determined. By a combination of these rate and molecular weight measurements with the identification of the volatile products of degradation, the essential features of the simpler degradation reactions were established. In particular the nature of depolymerization as a reverse polymerization reaction was appreciated and extensive studies of this kind, made especially at the National Bureau of Standards, showed for the first time how a variety of apparently different kinds of behaviour could be explained in terms of a single reaction mechanism.

More detailed studies of single polymers also illustrated at this time the influence of trace abnormalities in polymer structure in determining stability. The classical example, which was first demonstrated[3] in 1947, is

the fact that the depolymerization of poly(methyl methacrylate) at 200°C occurs through the unsaturated chain ends formed during polymerization. If these are eliminated the polymer is very much more stable.
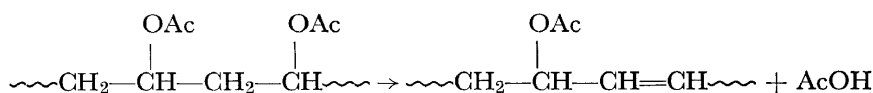
It was in these early days too that the value of model compounds in studying reactions in polymers was first appreciated. In the oxidation of rubber, for example, the hydroperoxide, carbonyl, hydroxyl and other oxygenated products being attached to the polymer molecule are extremely difficult to estimate by classical chemical methods. Using small unsaturated molecules the essential features of oxidation of this kind were demonstrated in great detail[4, 5].

The upsurge of interest in degradation at this time is reflected by the fact that a number of monographs [6-8] were published during the period in which the great majority of the references are post 1950.

Another reason for the development of interest at this time in the more fundamental aspects of degradation was the fact that the trial and error methods involved in the use of additive stabilizers were reaching the limits of their usefulness. It had become important to understand the chemical action of stabilizers so that they might be chosen more intelligently. The stabilizing action of antioxidants in unsaturated rubbers was certainly clarified by the studies of the mechanism of oxidation of unsaturated model compounds to which I have already referred[4, 5].

Poly(vinyl chloride) was even then one of the most important commercial polymers although also naturally the least stable in common use, its application being entirely dependent upon added stabilizers. Had it been discovered at the present stage of development of the plastics industry it would almost certainly be eliminated as useless because of its general instability to all the common degradation agencies. The intense interest which existed around 1950 in its degradation and in the mode of action of stabilizers is reflected by four papers which were presented at a symposium[6] on polymer degradation held in 1951. A great deal of useful information is contained in these papers but the great weakness, as with much of the work of the time, was the failure to recognize that the overall ageing process was due to a combination of degradative agencies which would have to be studied in isolation from one another for a proper understanding of the deterioration processes. This was clearly recognized in the more fundamental work on poly(vinyl chloride) which was published from 1954 onwards[9].

An additional factor which was important in directing the attention of chemists to polymer degradation processes was the fact that well known chemical reactions often assumed new features when they occurred in a polymer chain environment. The decomposition of simple esters of carboxylic acids into acid and olefin, for example, were known usually to be first order molecular processes. In poly(vinyl acetate), however, the olefinic centre being retained in the polymer chain,

$$\underset{\substack{| \\ \text{OAc}}}{\sim\!\!\sim\!\!\text{CH}_2\text{—CH}}\text{—CH}_2\text{—}\underset{\substack{| \\ \text{OAc}}}{\text{CH}}\!\!\sim\!\!\sim \rightarrow \sim\!\!\sim\!\!\text{CH}_2\text{—}\underset{\substack{| \\ \text{OAc}}}{\text{CH}}\text{—CH}\!\!=\!\!\text{CH}\!\!\sim\!\!\sim + \text{AcOH}$$

was found to facilitate the decomposition of the adjacent ester unit so that

the reaction moves from unit to unit along the chain, converting the simple reaction in model esters to an autocatalytic chain process in the polymer[10].

Similarly, the polymerization of nitrile groups is facilitated by a polymer chain environment. Simple nitriles do exhibit some slight tendency to polymerize—rather unstable cyclic trimers may be formed, for example
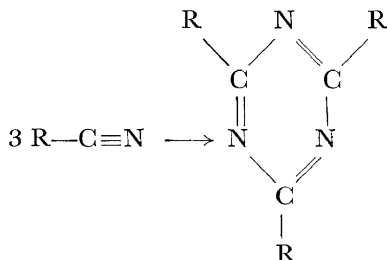
In polyacrylonitrile and polymethacrylonitrile, on the other hand, adjacent nitrile groups are in highly favourable positions for reaction and take part in a chain process in which conjugated sequences of increasing lengths are formed[11],
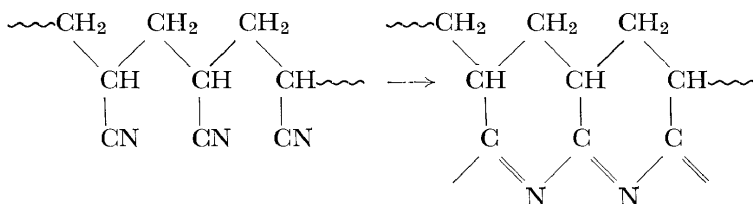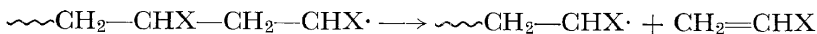

and which result in the deteriorative discoloration of these materials.

These were the kind of things which were being done and the ways in which workers were thinking in the degradation field around 1955. But by this time a number of new influences were making themselves felt in polymer chemistry. For example, extensive investigations were being made into the effects of high energy radiation on polymers[12-14]. Although this had at first promised great advances in the production of improved materials, the outcome has been disappointing. Nevertheless, it did promote a new interest in the effects of visible and ultraviolet radiation on polymers which plays such a vital part in ageing. Perhaps this approach was overshadowed by the discovery of stereospecificity, and all that it implies, which represented the most important advance in the whole of polymer science in the 1950s.
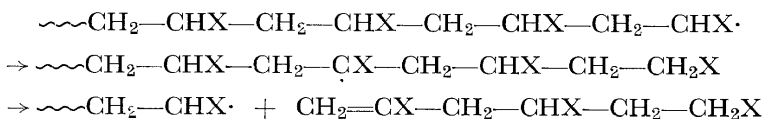
From the more limited point of view of polymer degradation, however, there seems to me to have been two vital stimulants to its vigorous development in the eight or nine years up to the present time. Firstly, there was the gradual realization that the most effective route to materials of greater stability was the building of molecules to specification using the fundamental results obtained from degradation studies. This approach will inevitably be given strong official support as a phase in the continuing search for heat resisting synthetic materials to help to solve, in particular, some of the problems of high speed and space flight. The second stimulus to progress in degradation studies depends upon the fact that, since 1945, a great variety

of new tools for chemical investigation have been developed which have revolutionized chemical analysis. Thus, within the past ten years ultraviolet, infrared, nuclear magnetic resonance, electron spin resonance and mass spectrometry, as well as vapour phase chromatography and various isotope techniques, have become freely available in polymer laboratories and have made it possible to solve problems of polymer structure, stability and degradation mechanisms which were hitherto beyond reach. The success achieved along these lines may be illustrated by a few examples.

The application of mass spectrometry to degradation problems is especially associated with Wall, Madorsky and their colleagues in a sustained series of researches over the past 15 years[15]. They have made detailed analysis of the products of degradation of a large selection of polymers and by combining these with rate measurements have been able to make interesting qualitative correlations between polymer structure and the kind of degradation reaction which occurs. Thus, broadly speaking, monomeric or non-monomeric chain fragments predominate depending upon whether the degrading free radical tends to depolymerize

$$\sim\sim CH_2—CHX—CH_2—CHX\cdot \longrightarrow \sim\sim CH_2—CHX\cdot + CH_2{=}CHX$$

or undergo transfer reactions

$$\sim\sim CH_2—CHX—CH_2—CHX—CH_2—CHX—CH_2—CHX\cdot$$

$$\rightarrow \sim\sim CH_2—CHX—CH_2—CX—CH_2—CHX—CH_2—CH_2X$$

$$\rightarrow \sim\sim CH_2—CHX\cdot + CH_2{=}CX—CH_2—CHX—CH_2—CH_2X$$

and these can clearly be related both to radical reactivity and the reactivity of potentially transferable atoms attached to the polymer chains. Thus the pattern of degradation products can yield a great deal of fundamental information. More recently, as polymer stability at elevated temperatures has become of particular interest, this group of workers, using the same techniques, have illustrated how the pattern of degradation products changes as the degradation temperature is extended up to 1200°C. Their data[16] for polymethylenes are reproduced in *Table 1*, which illustrates in particular how fragmentation increases as the degradation temperature is
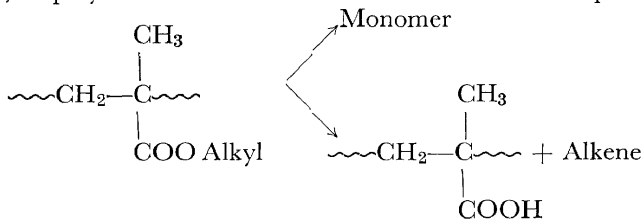
Table 1. Volatiles from pyrolysis of polymethylene

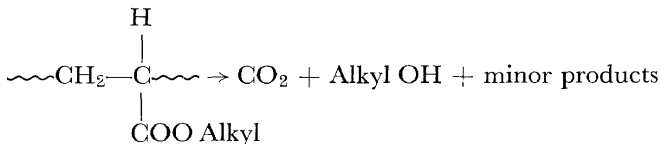| Product	Weight % of total volatiles		
	500°C	800°C	1200°C
H_2	—	0·1	0·2
CH_4	—	0·1	3·6
C_2H_2	—	—	3·3
C_2H_4	—	5·5	26·4
C_2H_6	0·1	0·3	0·9
C_3H_4	0·1	0·2	2·7
C_3H_6	0·1	2·9	8·0
C_3H_8	0·2	—	0·5
C_4H_6	0·3	0·9	7·1
C_4H_8	0·3	3·9	3·1
C_5–C_8	4·8	8·3	2·9
Involatile at room temperature	94·1	77·8	41·3

raised. These results are typical of detailed analysis which they have been able to achieve.

Vapour phase chromatography can give the same kind of analytical results, often very much more simply, and is being used extensively. While the decomposition of polymethacrylates by two competing mechanisms, namely, depolymerization to monomer and ester decomposition, is now

$$\begin{array}{c}
CH_3 \\
| \\
\sim\sim CH_2\!-\!C\!\sim\sim \\
| \\
COO\ Alkyl
\end{array}
\quad
\begin{array}{l}
\nearrow \text{Monomer} \\
\\
\\
\searrow \quad
\begin{array}{c}
CH_3 \\
| \\
\sim\sim CH_2\!-\!C\!\sim\sim \ +\ Alkene \\
| \\
COOH
\end{array}
\end{array}$$

well understood[9] it has long been known that acrylates do not behave in this way in spite of the similarity in structure. Instead, carbon dioxide and the corresponding alcohol are the main products, together with a variety of materials in smaller yield.

$$\begin{array}{c}
H \\
| \\
\sim\sim CH_2\!-\!C\!\sim\sim \rightarrow CO_2\ +\ Alkyl\ OH\ +\ minor\ products \\
| \\
COO\ Alkyl
\end{array}$$

Precise analyses of these products using vapour phase chromatography are, at the present time, enabling the acrylates to be fitted into the general picture of the decomposition of acrylic polymers[17].

A very much more sophisticated application of vapour phase chromatography, which may be an indication of important future developments, is illustrated by the paper by Robb and his colleagues which is before this conference and which shows how the technique may be used directly as a tool for kinetic studies.

There have been a number of examples in which the influence of isotopic substitution, particularly of deuterium for hydrogen, on degradation reactions has given useful information about reaction mechanism. However, one of the potentially most valuable examples of isotopic work is perhaps that recently published by McNeill[18] who has developed a method whereby unsaturated structures may be estimated by reacting with ^{36}Cl and estimating the activity of the resulting polymer by conventional methods. This is especially important because traces of unsaturated structures, usually built into the polymer during the polymerization process, are frequently the cause of instability—they can serve as centres of initiation for radical degradation processes by weakening adjacent bonds because of the allylic resonance stabilization in the resulting radical.

$$\sim\sim C\!=\!C\!-\!C\!-\!C\!-\!C\!\sim\sim \longrightarrow \sim\sim C\!=\!C\!-\!C\cdot\ +\ \cdot C\!-\!C\!\sim\sim$$
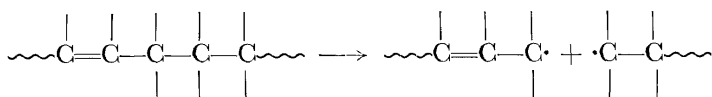
More recently it has been found possible to estimate concentrations of less

than one double bond per molecule of isobutylene with a molecular weight of 600,000 and to distinguish between terminal and main chain unsaturation in polystyrene[19].

Infrared spectroscopy is perhaps the oldest and certainly the most widely applied of these modern analytical methods and the range of degradation problems which it has helped to solve is wide indeed. Two examples taken from studies of the thermal degradation of polymethacrylonitrile will serve to illustrate its usefulness. The first is concerned with the mechanism of the thermal coloration of this polymer. It was found that the rate at which coloration occurs is roughly proportional to the height of the carbonyl band at 1720 cm^{-1} in the infrared spectrum of the parent material[20]. The carbonyl band is due to acidic impurities built into the polymer chains but, as coloration develops, a shoulder first appears on the 1720 cm^{-1} peak at 1693 cm^{-1} as shown in *Figure 1* becoming more intense than the original band at advanced stages of degradation[21]. At the same time the nitrile peak at 2210 cm^{-1} decreases in intensity and broad absorption develops in the region 1660–1500. This has been interpreted as being due to the internal polymerization of nitrile groups in the following sequence:
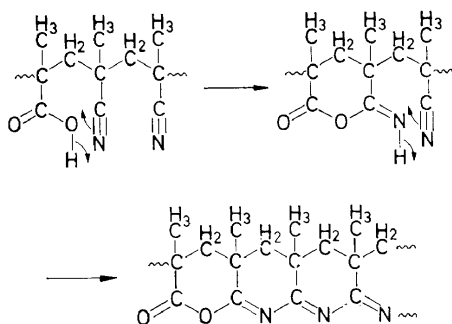
absorption at 1693 cm^{-1} and in the region 1660–1500 cm^{-1} being due to C=N and conjugated carbon–nitrogen sequences respectively.

In *Figure 1* absorption at 2012 cm^{-1} is seen to disappear in the early stages of the reaction. This band is due to ketene–imine structures built into the polymer during its preparation by reaction of the growing radical in its alternative form:
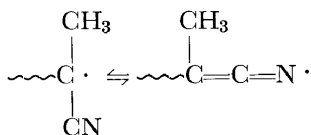
and it was found possible to follow the kinetics of decomposition of these structures in solution at 90°C using the intensity of absorption as a measure of their concentration with the neighbouring nitrile peak as a convenient reference[22] as shown in *Figure 2*.

As well as providing direct chemical evidence, nuclear magnetic resonance spectroscopy has been found to be particularly useful for investigating
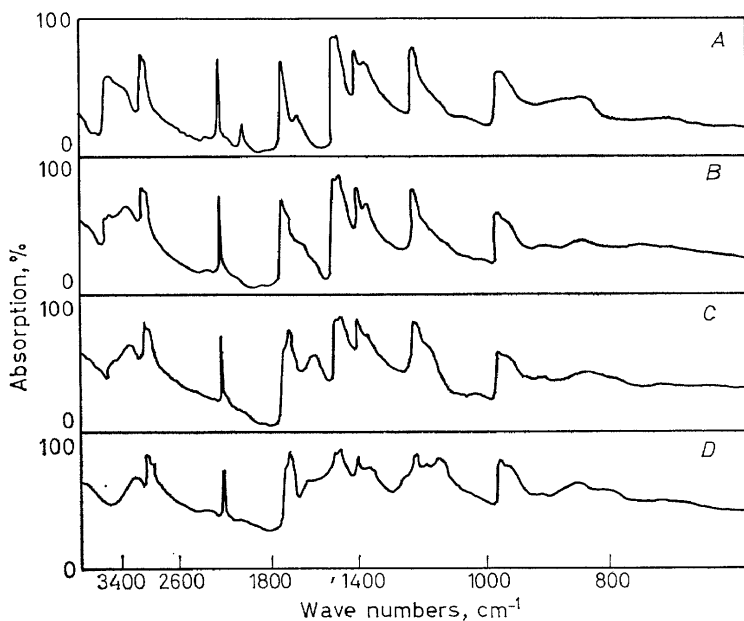
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Figure 1. Changes in infrared spectrum of polymethacrylonitrile during colouration at 140°C:
A, undegraded, colourless; B, 3 hours, yellow-orange; C, 9 hours, orange-red; D, 23·5 hours,
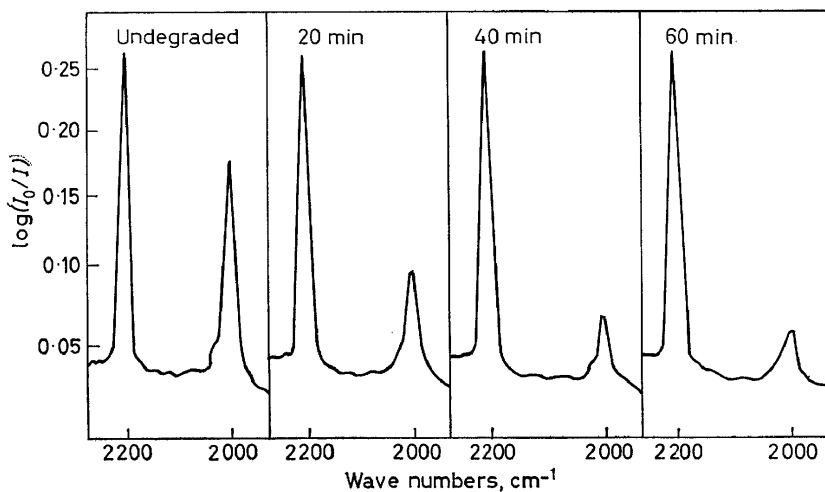deep red

Figure 2. Disappearance of ketene–imine absorption at 2012 cm^{-1} on heating polymetha-
crylonitrile in cyclohexanone solution at 90°C

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problems associated with the physical structure of polymers. A recent paper by Neiman and his co-workers[23], for example, has made use of the fact that the NMR absorption of polypropylene can be separated into a broad and a narrow component which are due to protons in the crystalline and amorphous regions respectively. By studying the changes which occurred in these two components during the course of thermal-oxidative degradation they were able to show that while the polymer becomes more amorphous during degradation, there is no change in the internal motions of the crystalline regions and this would seem to imply that oxidation does not occur uniformly throughout the polymer but in the amorphous regions and at the crystalline boundaries.

In the past, positive evidence about the structure of the radicals involved in chemical reactions has been virtually impossible to obtain and at best information has been deduced indirectly from the kinetic features of the reaction. Once electron spin resonance spectroscopy becomes widely available as a routine tool in laboratories it should therefore be widely applicable to polymer degradation reactions, the majority of which are radical processes. Two recent papers illustrate the kind of information which has been obtained for relatively simple polymers. Irradiation of polypropylene[24] by γ-rays from ^{60}Co might reasonably be expected to result in scission at the tertiary C—H bond to give radicals A. However only

$$
\begin{array}{cc}
\overset{\displaystyle CH_3}{\underset{\displaystyle \cdot}{\overset{\displaystyle |}{\sim\!\sim\!CH_2-\overset{}{C}-CH_2\!\sim\!\sim}}} & \overset{\displaystyle \dot{C}H_2}{\underset{}{\overset{\displaystyle |}{\sim\!\sim\!CH_2-CH-CH_2\!\sim\!\sim}}} \\[2em]
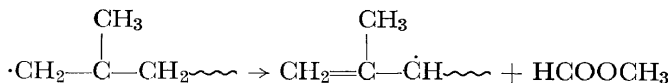A & B
\end{array}
$$

20 per cent are found to be of this type, the majority having the structure B.

Perhaps more surprising is the fact that γ-irradiation of poly(methyl methacrylate) and the polymerization of methyl methacrylate by a variety of methods[25] always yields the same two radicals, C and D.

$$
\begin{array}{cc}
\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{\sim\!\sim\!CH_2-C\,\cdot}}}} & \overset{\displaystyle CH_3}{\underset{}{\overset{\displaystyle |}{CH_2\!=\!C-\dot{C}H\!\sim\!\sim}}} \\[3em]
C & D
\end{array}
$$

C is expected by chain scission and during polymerization but D must be a secondary product, possibly being formed in the case of irradiated polymer by disproportionation of the other product of chain scission,

$$
\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\cdot CH_2-C-CH_2\!\sim\!\sim}} \rightarrow \overset{\displaystyle CH_3}{\overset{\displaystyle |}{CH_2\!=\!C-\dot{C}H\!\sim\!\sim}} + HCOOCH_3
$$

Alongside these modern techniques, the older methods of studying polymer degradation are undergoing development. For example, by combining the technique of temperature programming as used in thermogravimetric work with the measurement of the development of pressure over degrading

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polymer one can obtain a continuous measurement of rate which amounts to a "thermal" spectrum which is quite characteristic of any polymer[26]. *Figure 3* shows how two samples of poly(methyl methacrylate) prepared
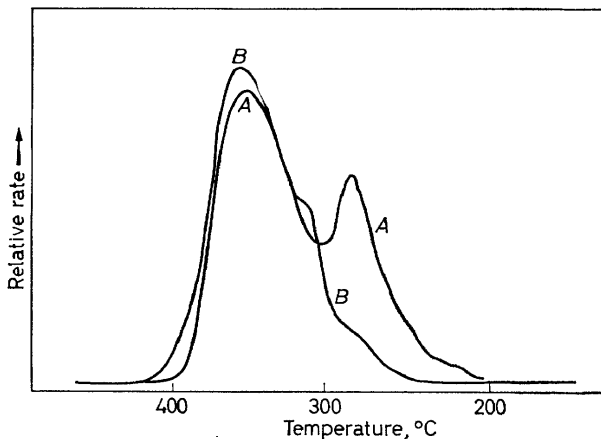

Figure 3. Thermal spectra of poly(methyl methacrylate): *A*, radical; *B*, ionic

by different methods can be distinguished.The differences can be accounted for in terms of known mechanisms of degradation, the lower temperature peak in the radical polymer being the result of degradation through the unsaturated chain ends which are absent in the ionic polymer. The different stabilities of poly(vinyl chloride) and poly(vinyl acetate) can be seen in *Figure 4* but the fact that the residues, after the loss of the corresponding acids, are the same, namely
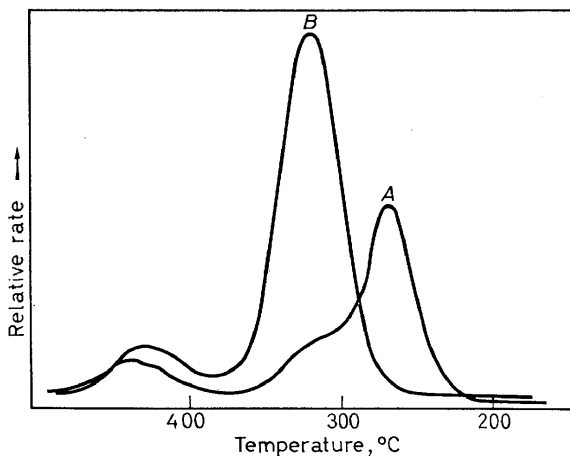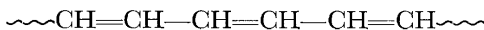
$$\sim\!\!\sim\!\!CH\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH\!\!\sim\!\!\sim$$

Figure 4. Thermal spectra of *A*, poly(vinyl chloride); *B*, poly(vinyl acetate)
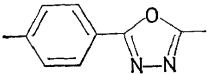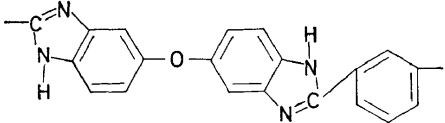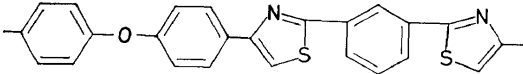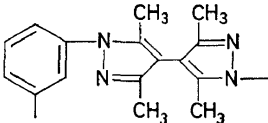
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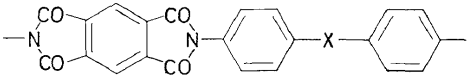
is confirmed by the fact that the higher temperature peaks are identical.

By comparison with the traditional methods of chemical analysis, each one of these new techniques is extremely powerful and widely applicable and although, in the past 10 years, they have made it possible to examine polymer degradation problems which would previously have been insoluble their full potentiality has not yet been applied. This is largely due to their limited availability in laboratories which, in turn, has usually resulted in their being used in isolation from each other.

Looking through the polymer degradation literature we can see that to the present time individual laboratories have had outstanding success through the application of one or other of these techniques. One can think of laboratories which have made their reputations in this field by the application of mass spectrometry or infrared spectroscopy or which are rapidly building up reputations by the application of nuclear magnetic resonance or electron spin resonance. With greater availability it will be possible for laboratories to study problems using combinations of these techniques and already one can see signs in the literature of the development of this phase. In this way the many outstanding problems of degradation mechanism and the role of stabilizers as well as the relationships between stability and physical and chemical structure will be more effectively studied.

The present state of development and availability of these new techniques is important from another point of view, however. I said earlier that in addition to the influence of new techniques, polymer degradations studies had been stimulated during the past 8 or 9 years by the search for heat

Table 2. Some recently synthezised high temperature polymers

Polymer	Reference
	27
	28
	29
	30
	31

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resisting synthetic materials. The efforts which have been made in this direction are now showing their rewards. Hitherto, the emphasis has been on synthetic methods but the principal structural features for high stability are now much better understood and a large number of materials are becoming available for characterization and assessment of potential usefulness. A few of the many which have recently been synthesized and for which claims of high temperature stability are made are illustrated in *Table 2*. They give some idea of the chemical complexity which makes the synthesis of these materials so time consuming and expensive. It is therefore all the more important that degradation studies should play their full part in the production of better materials by giving back to the synthetic chemist as much information as possible about the decomposition of his products so that he can use this information in planning further synthesis. It is obvious from the structures of these materials that investigations of the mechanisms of their breakdown are probably going to be difficult. It is in this connection that the development of the new analytical methods seems to be timely and could, in the near future, lead to the most spectacular advances in the study of polymer degradation.

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