POLYMER DEGRADATION AND ELECTRON SPIN RESONANCE SPECTROSCOPY

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Two years ago, at the symposium in Prague, I chose as the theme of a lecture similar to this one, the application of modern analytical techniques to the solution of polymer degradation problems[1]. I tried to demonstrate some of the contributions which had been made by the use of, for example, infrared, mass and nuclear magnetic resonance spectroscopy as well as gas chromatography and radiochemical techniques. I looked forward to rapid developments in the utilization of such methods and especially to the simultaneous application of a number of them in order to try to solve some of the more difficult problems of polymer degradation.

One of the techniques to which I made brief reference at that time was electron spin resonance spectroscopy. Of all the modern analytical techniques, e.s.r. is probably most limited in its application in the sense that it is concerned only with free radicals. On the other hand information about free radicals cannot be obtained in any other comparably direct way and its potential value in the study of polymer degradation processes is clear since so many of them proceed by free radical mechanisms. During recent years, limited but definite progress has been made in the application of e.s.r. to polymer degradation problems and its was against this background that the organizers of this conference invited me to talk on the subject of "Electron Spin Resonance and Polymer Degradation".

Since I am certainly not competent to make authoritative judgements upon the interpretation of e.s.r. data, I had to assume that I was invited to this task because of my interest in polymer degradation. In order to emphasize this fact, I have reversed the title originally suggested so that it now reads "Polymer Degradation and Electron Spin Resonance". It is my intention to review progress in the application of e.s.r. data to polymer degradation, aiming my lecture especially at the majority of you who, I hope, like myself, would like to learn something of the potentiality of the technique in this direction. My intention is to try to stimulate interest rather than give an authoritative review. Firstly, I shall discuss briefly and quite generally the kind of information which e.s.r. measurements can give. Secondly, I shall describe some of the results from the literature which have interested me. Finally, I shall discuss polymer degradation problems in which I am currently interested and to which e.s.r. might be relevant.

Electron spin resonance spectra are associated with the unpaired electrons which exist in free radicals[2]. An electron may only have a spin, m_s, of either $+\frac{1}{2}$ or $-\frac{1}{2}$ so that when a magnetic field, H, is applied to a system containing free electrons they will become aligned with their spins parallel

or antiparallel to the magnetic field. The energies of the two kinds of electrons are $\frac{1}{2}g\mu H$ above and below their energies in absence of an applied field, μ being a constant and g a variable factor depending upon the interaction of the unpaired electron with the rest of the system. Thus, an energy transition of magnitude $h\nu = g\mu H$ is possible within the system, as illustrated in the second step of *Figure 1*. Clearly, absorption of radiation can take place at any frequency depending upon field strengths but high sensitivity is obtained at high field strengths and in practice the field strength and the
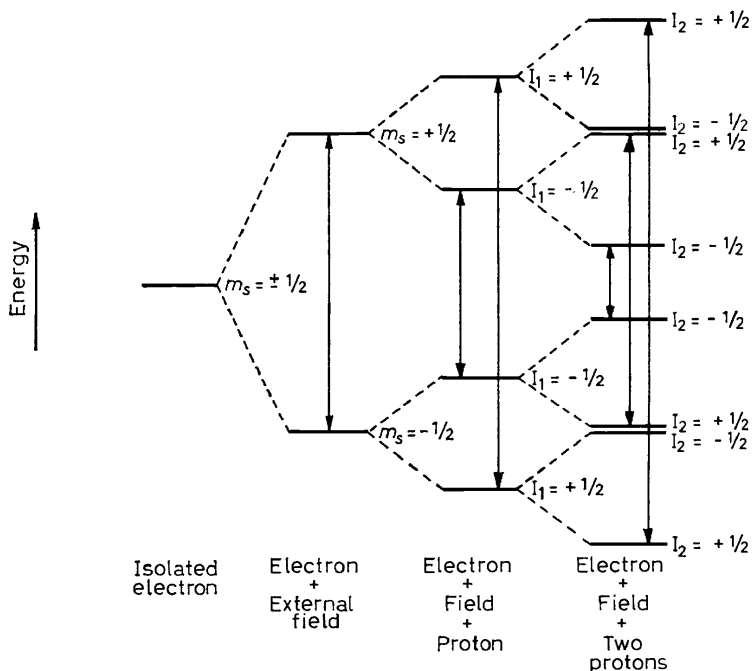

Figure 1. Hyperfine splitting of energy levels by protons

frequency of the applied radiation are only limited by the problems of instrument design. Resonance absorption could obviously be detected by maintaining the field constant and varying frequency or by maintaining constant frequency and scanning the field. For various reasons, the latter is preferred and all commercial instruments are based on this principle. Frequencies of the order of 10 000 Mc/s and magnetic fields up to 5000 gauss are used. The area under the absorption curve is directly proportional to the concentration of free radicals. It turns out that the value of g does not vary very much with the environment of the free radical so it is difficult to derive information about the nature of the radicals involved from the position of absorption in the e.s.r. spectrum as shifts in nuclear magnetic resonance spectra can give information about the environment of protons. The real source of information is the well-defined and characteristic hyperfine splitting which can occur.

If the unpaired electron finds itself in the environment of one atomic nucleus possessing spin, there will be interaction between their magnetic fields. In the case of a proton, which has a spin (I) of $\pm\frac{1}{2}$, the spins will be aligned, in the applied magnetic field, parallel or antiparallel to each other and the various energy levels may be represented as in the third step in *Figure 1*. Since the nuclear spins remain unchanged during the electron spin resonance transition, only the energy transitions indicated are possible and two peaks will appear in the e.s.r. spectrum. This is described as *hyperfine splitting*. The magnitude of the splitting is obviously a direct measure of the interaction between electron and nucleus and can thus often give a great deal of information about the location of a free radical centre.

When an unpaired electron is equally coupled with a second proton, the energy level diagram may be extended as illustrated in the fourth step in *Figure 1*. Three transitions are now clearly possible, which are represented by three equally spaced spectral lines with intensities in the ratio $1:2:1$. In general, for n equivalent protons the number of lines is $2nI + 1$ with intensities proportional to the coefficients of the binomial expansion. Very much more complicated spectra arise when, for example, the nuclei are not all magnetically equivalent with respect to the unpaired electron or when different kinds of nuclei are involved. A typical e.s.r. absorption spectrum is illustrated in *Figure 2a*. It refers to the $\cdot CH_2OH$ radical obtained by irradiating methanol. Spectra are usually represented, however, in the form of the first derivative as in *Figure 2b*.
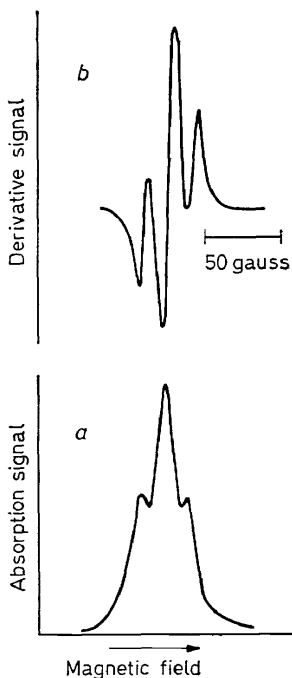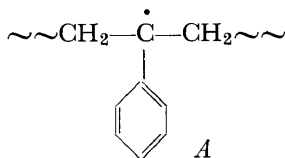

Figure 2. Electron spin resonance spectrum of irradiated methanol, after Fijimoto and Ingram[24] and Willard, Merritt and Dean[2]

The problems of detecting and identifying radicals in chemical reactions are intensified by reason of their low concentration, which is a direct result of their high reactivity. Concentrations can be increased by increasing the lifetime of the radicals and it is for this reason that a great many e.s.r. investigations have been carried out on radicals immobilized or trapped in the solid phase. Radicals are most readily formed in such an environment by high energy irradiation and indeed we can discern the birth of the modern interest in e.s.r. as being closely associated with the interest in the chemical effects of high energy radiation which developed rapidly after powerful sources of high energy radiation became available about 20 years ago. Part of this interest was strongly focused upon polymers and its relevance to the wider aspects of polymer degradation was obvious since at that time a number of degradation reactions had been shown to proceed by free-radical mechanisms. Since that time to the present, e.s.r. spectroscopy has demonstrated clearly the kinds of radicals which are to be expected in degrading polymers.

Evidence from e.s.r. spectra of γ-irradiated polystyrene, for example, gives support to the assumption that radicals with the structure A are

$$\sim\sim CH_2\text{---}\overset{\bullet}{C}\text{---}CH_2\sim\sim$$

A

involved in the photolysis and photo-oxidation of polystyrene[3]. Polystyrene irradiated at 77°K *in vacuo* gives a three-line spectrum, as in *Figure 3*[4].
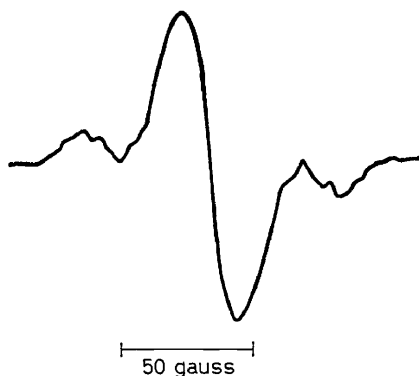

|———————————————|
50 gauss

Figure 3. Electron spin resonance spectrum of polystyrene irradiated at 77°K and observed at 300°K, after Florin, Wall and Brown[4]

Abraham and Whiffen[5] believed it to be due to interaction of the unpaired electron in A with two of the four adjacent methylene protons. This was disputed by Tsvetkov, Molin and Voyevodskii[6] who believed that the radical centre is on the benzene ring. The problem was resolved by Florin, Wall and Brown[4], however, who demonstrated that neither deuterium

substitution in the main chain nor substitution in the *meta-* and *para-*positions in the ring affect the spectrum but that *ortho-*substitution changes it completely (*Figure 4*). The only possible explanation of these observations is that the radical has the structure *A* and that the three-line spectrum is the result of interaction of the unpaired electron with the two *ortho-*protons. This spectrum is maintained on warming the polystyrene to room temperature although over a prolonged period changes occur which suggest the development of interaction of the unpaired electrons with the chain protons[7]. The nature of these changes is not precisely understood but seems worthy of re-examination in the light of what is now known about the mechanisms of thermal and photo-degradation of polystyrene.


50 gauss

Figure 4. Electron spin resonance spectrum of poly(2,5-dichlorostyrene) irradiated at 300°K and observed at 300°K, after Florin, Wall and Brown[4]

The high-energy irradiation of polyethylene has been shown to result in three different radicals[8]. A sextet spectrum, associated with a relatively stable radical, has been attributed to the alkyl radical,

$$\sim\sim CH_2 - \overset{\displaystyle\cdot}{C}H - CH_2 \sim\sim$$

A more complicated spectrum, probably a septet of doublets, has been associated with the more stable allyl radical,

$$\sim\sim CH_2 - \overset{\displaystyle\cdot}{C}H - CH = CH \sim\sim$$
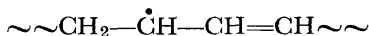
Finally, a very stable radical with a singlet spectrum is believed to be polyenic

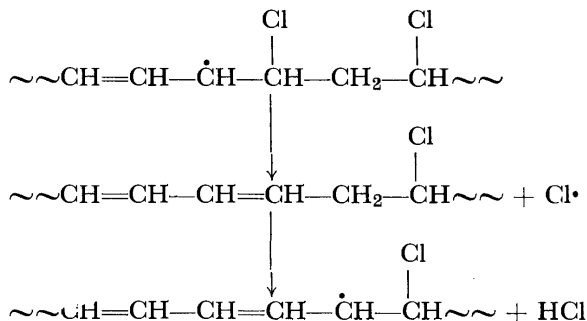$$\sim\sim CH_2 - \overset{\displaystyle\cdot}{C}H - (CH = CH)_n - CH_2 \sim\sim$$

The alkyl radical predominates in polymer lightly irradiated (<1 Mrad) at low temperatures. With intermediate doses (10–100 Mrad) the allyl radical predominates while even higher doses give the polyene which is quite stable for long periods at room temperature. Grishina and Bakh[9] claim that,
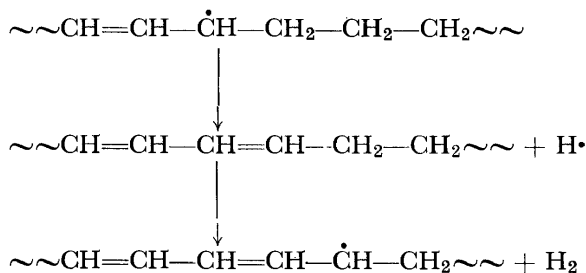
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at dosages greater than 6000 Mrad, cyclic polyenic structures become involved.

These observations are relevant to more conventional polymer degradation studies because they clearly indicate that under the influence of high-energy irradiation, polyethylene can be made to eliminate hydrogen from series of adjacent ethylene units to form a polyene structure in very much the same way as poly(vinyl chloride) eliminates hydrogen chloride. Indeed, the mechanism in polyethylene must be strictly analogous to that proposed for poly(vinyl chloride)[10], the propagation steps of the chain process being,
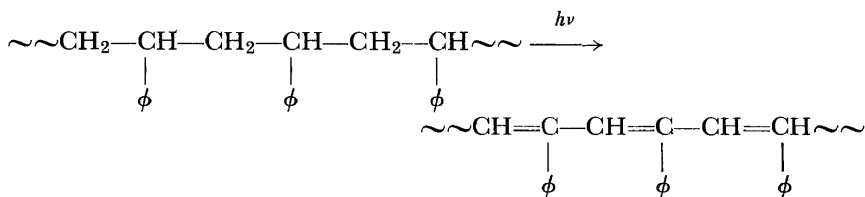
for poly(vinyl chloride)

$$\sim\sim CH=CH-\overset{\bullet}{C}H-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}H\sim\sim$$

$$\downarrow$$

$$\sim\sim CH=CH-CH=CH-CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}H\sim\sim \ + \ Cl\bullet$$

$$\downarrow$$

$$\sim\sim CH=CH-CH=CH-\overset{\bullet}{C}H-\overset{\overset{\displaystyle Cl}{|}}{C}H\sim\sim \ + \ HCl$$

for polyethylene

$$\sim\sim CH=CH-\overset{\bullet}{C}H-CH_2-CH_2-CH_2\sim\sim$$

$$\downarrow$$

$$\sim\sim CH=CH-\overset{|}{C}H=CH-CH_2-CH_2\sim\sim \ + \ H\bullet$$

$$\downarrow$$

$$\sim\sim CH=CH-CH=CH-\overset{\bullet}{C}H-CH_2\sim\sim \ + \ H_2$$

It is interesting that hydrogen is believed to be similarly eliminated from the chain backbone of polystyrene by ultraviolet irradiation[11],

$$\sim\sim CH_2-\underset{\phi}{\overset{|}{C}}H-CH_2-\underset{\phi}{\overset{|}{C}}H-CH_2-\underset{\phi}{\overset{|}{C}}H\sim\sim \ \xrightarrow{h\nu}$$

$$\sim\sim CH=\underset{\phi}{\overset{|}{C}}-CH=\underset{\phi}{\overset{|}{C}}-CH=\underset{\phi}{\overset{|}{C}}H\sim\sim$$

This kind of reaction, which was regarded as an almost exclusive property of poly(vinyl chloride) and related chlorine-containing and vinyl-ester

polymers, is now seen to be typical of a wider range of vinyl polymers. This series, poly(vinyl chloride), polystyrene, polyethylene is interesting to speculate upon from the general point of view of polymer degradation.

A great deal of attention has been given to radicals derived from poly-(methyl methacrylate). Nevertheless, profound differences of opinion exist about the interpretation of their e.s.r. spectra and this system serves to illustrate the care which will have to be taken in the application of this technique to the clarification of polymer degradation mechanisms. Radicals produced at room temperature by a variety of methods, including γ-ray, x-ray and u.v. irradiation and occluded during polymerization in gelled or precipitated polymers, give an identical nine-line spectrum [12-14] which is
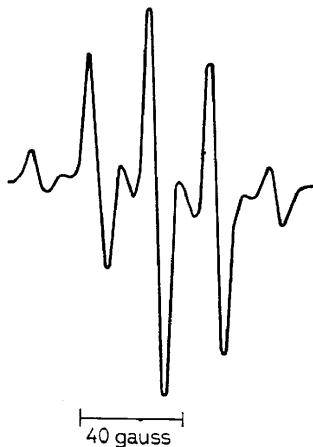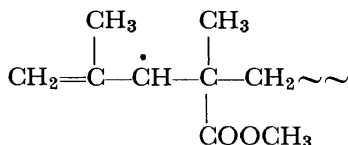

40 gauss

Figure 5. Electron spin resonance spectrum of poly(methyl methacrylate) irradiated and observed at room temperature, after Kourim and Vacek[15]

illustrated in *Figure 5*[15]. There has been general agreement that this is composed of overlapping five- and four-line spectra. The point in question is whether they arise from a single radical or from two different radicals. By comparison with the corresponding spectra of other methacrylates[13, 16] and of various deuterated poly(methyl methacrylates)[15] it has been deduced that the two overlapping spectra are derived from the single radical, *B*.

$$\sim\sim CH_2 - \overset{\overset{\displaystyle CH_3}{\displaystyle |}}{\underset{\underset{\displaystyle COOCH_3}{\displaystyle |}}{C}}\cdot \qquad B$$
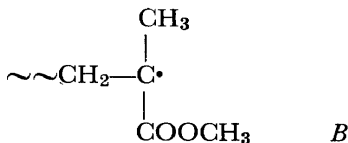
The ester methyl protons are not involved but interaction of the five β protons with the unpaired electron is limited by rotational restrictions so that interaction can occur with only either three or four thus leading to the composite nine-line spectrum. The balance of present opinion favours this theory rather than Bullock and Sutcliffe's suggestion[17] that while the five-

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line spectrum arises from the above alkyl radical, the four-line spectrum is due to the allyl radical

$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}\overset{\displaystyle \bullet}{C}H{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}{-}CH_2\sim\sim$$

Ambiguities which might arise in the application of e.s.r. data of this kind to degradation mechanism problems become evident when the spectra obtained by irradiation at different temperatures are compared. The evidence is that irradiation at 77°K causes scission of the ester group so that the rather complicated spectrum is due to the radical ·COOCH₃ and perhaps ·CH₃ and ·CHO[18]. As the temperature of the sample is raised the spectrum gradually becomes converted to the nine-line spectrum obtained by irradiation at a higher temperature. It is also interesting that, even at the higher temperatures, monomer is required to be present for the proper resolution of the nine-line spectrum[18, 19]. It seems, therefore, that while the nine-line spectrum of radical B will normally be detectable in degrading poly(methyl methacrylate) it must not be assumed that the initiation process is main-chain scission. Elimination of side chains is more likely, to be followed by a secondary decomposition process which results in the radical B.

With the development of the e.s.r. technique, and especially if its sensitivity can be increased, work of this kind, carried out on polymers in the act of degrading under the influence of heat, visible and ultraviolet radiation and during oxidation, clearly has great potential in the clarification of degradation mechanisms. However, as I said in the conclusion of my lecture in Prague two years ago, these modern analytical techniques will be most effective when they are so widely available that they can be used in combination with each other. Some recent studies on poly(vinyl chloride), in which e.s.r. and u.v. and visible spectroscopy have been applied in combination may be a signpost for the future.

A number of laboratories have investigated this system. The fact that their conditions of irradiation and subsequent observation of e.s.r. spectra vary from one to another, places a limitation on the close comparison of their results. It is nevertheless possible to see how e.s.r. spectral evidence can contribute to a more complete understanding of the degradation of poly-(vinyl chloride). The changes which occur in the e.s.r. spectrum as the temperature of previously irradiated polymer is raised are highly significant. Ohnishi and his coworkers[20] have obtained the series of spectra illustrated in *Figure 6*. The rather complicated spectrum (A) recorded at −196°C after irradiation at −196°C changes even on warming to −78°C (B). By subtracting (B) from (A) they have obtained a well-defined six-line spectrum and therefore suggest that the changes which occur in this temperature range are due to the disappearance of the radical, $\sim\sim CH_2{-}\overset{\displaystyle \bullet}{C}H{-}CH_2\sim\sim$. During storage at 20°C the spectrum changes progressively to a well-defined singlet while colour develops. Loy[21] and Atchison[22], on the other hand, have been more interested in the changes in radical concentration which
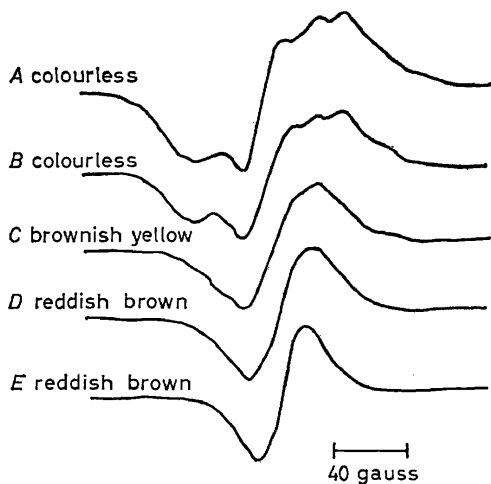
Figure 6. Change of electron spin resonance spectrum of poly(vinyl chloride), irradiated *in vacuo* at −196°C, with rising temperature, after Ohnishi, Nakajima and Nitta[20]: *A*, immediately after irradiation; *B*, after 15 hours at −78°C; *C*, after 5 minutes at 20°C; *D*, after 23 hours at 20°C; *E*, after 12 days at 20°C. Spectra recorded at −196°C
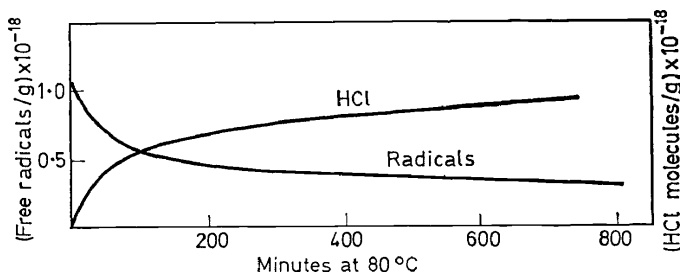

Figure 7. Change in free-radical concentration and HCl produced with time at 80°C of poly(vinyl chloride) previously irradiated at 77°K, after Loy[21]

occur at higher temperatures up to 80°C. They have shown firstly, as in *Figure 7*, that the decay in the concentration of free radicals at 80°C runs closely parallel with the evolution of HCl and secondly, as in *Figure 8*, that there are three distinct phases in the radical decay which can be attributed to three distinct types of radical. It is also clear from *Figure 8* that the amount of HCl produced per radical disappearing is characteristic of the radical. From this and other evidence, Loy has concluded that the rate of radical decay is a measure of the rate of initiation of the dehydrochlorination process and that the rate of evolution of HCl is a direct measure of the chain length in each case. From the data in *Figure 8* he derived chain lengths of 26, 51 and 126 for the short, medium and long lived radicals, respectively.

The development of colour, as well as the evolution of HCl, runs parallel with the change in radical concentration. Atchison[22] has been able to show
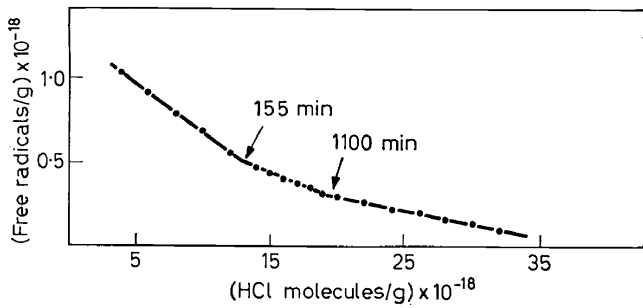
Figure 8. Relationship between free-radical concentration and HCl produced from poly(vinyl chloride) previously irradiated at 77°K, after Loy[21]

that the changes in the optical spectrum, illustrated in *Figure 9*, can be interpreted as a series of sharp peaks superimposed on a broad absorption band. The sharp peaks are clearly due to conjugated polyene sequences of various lengths and the magnitude of the broad band is closely related to the concentration of long lived radicals. While no firm conclusions about the
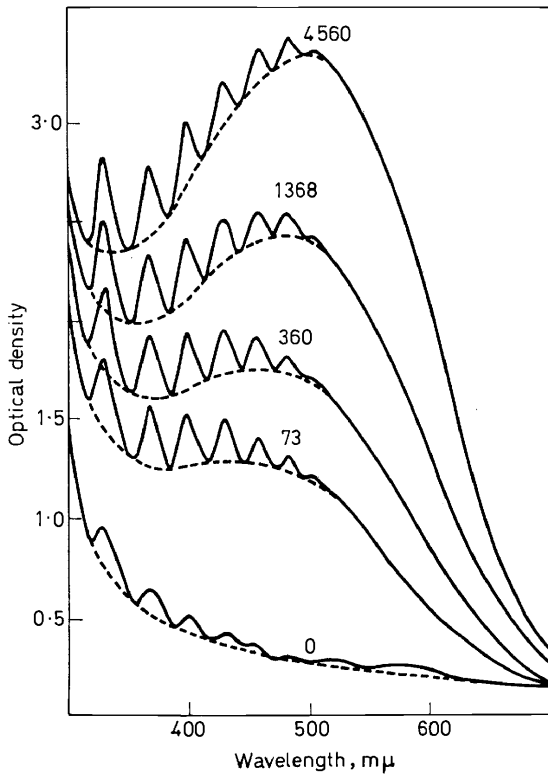

Figure 9. Development of colour in poly(vinyl chloride) during storage at 30°C after irradiation at room temperature, after Atchison[22]. Numbers on curves denote hours at 30°C

nature of the radicals involved or the precise mechanisms of these reactions are yet possible, these kinds of observations clearly illustrate the potential of e.s.r. in the polymer degradation field.

In most work which has been reported in which e.s.r. spectral data have been correlated with reactions in polymers the radicals have been produced at or below normal temperatures by means of high energy radiation and, as in the case of poly(vinyl chloride), it is the subsequent reactions of these radicals which have been studied. Although in many cases, and certainly in the case of poly(vinyl chloride), the overall characteristics of these reactions are similar to those which occur in thermal and photo-initiated degradations it is not at all certain that this is invariably so. Even in an apparently favourable case like poly(vinyl chloride) it is clear that important differences may exist between the mechanisms of the reactions brought about in these different ways. An immediate aim of e.s.r. spectroscopy in this field of study must, therefore, be to observe radicals during the course of thermally and photochemically induced degradation processes. There will be considerable experimental difficulty in carrying out degradation reactions at high temperature or under high light intensities within the spectrometer itself and simultaneously detecting relatively low radical concentrations, but if these problems can be overcome there is no doubt that vitally interesting information would be forthcoming. A great many of the conclusions which have been drawn about degradation processes from kinetic observations could be verified by direct identification of the radicals involved. I can probably best illustrate the kind of application I have in mind by devoting the remainder of this lecture to describing some recent work, the conclusions from which would be very much more convincing if they could be confirmed by e.s.r. data. This work concerns a comparison of the mechanisms of the thermal and photo–degradation of copolymers of methyl methacrylate and acrylonitrile[23].

The thermal reaction was studied at 280°C and the photo reaction at 160°C. As in pure poly(methyl methacrylate) the reactions consist basically of the depolymerization or "unzipping" of the polymer molecule to give monomer as the main product. Unlike the reaction in poly(methyl methacrylate) however, there is a rapid decrease in the molecular weight of the residual polymer. The presence of the acrylonitrile modifies the reaction in a different way in each case.

At the higher temperature of the thermal reaction the volatile product consists of a mixture of the two monomers although the proportion of acrylonitrile is less than in the copolymer. This demonstrates that the depolymerization process can pass through acrylonitrile units. Contrary to expectations the rapid decrease in molecular weight is not the result of scission at the acrylonitrile units. Indeed, *Figure 10* demonstrates that the rate of decrease of molecular weight is greater the lower the acrylonitrile content. The reaction in fact consists of random chain scission in the methyl methacrylate segments of the copolymer molecules to give radicals and this is followed by depolymerization which may pass through several acrylonitrile units before termination occurs, probably by interaction of pairs of radicals.

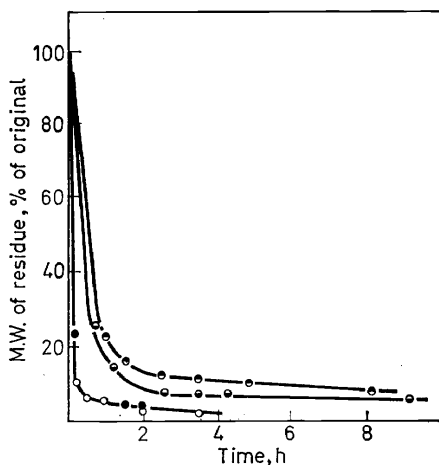In the photo-reaction, on the other hand, the rate of bond scission,

Figure 10. Changes in molecular weight with time, at 280°C, of methyl methacrylate/acrylonitrile copolymers (○, 410/1; ●, 40/1; ◓, 16/1; ◑, 8/1)

calculated from the decrease in molecular weight, increases with acrylonitrile content as illustrated in *Figure 11*. By contrast with the thermal reaction acrylonitrile is not liberated in detectable amounts. Thus, the photo-reaction consists of chain scission at or near the acrylonitrile units, followed by depolymerization to the next acrylonitrile unit. It is clear from *Figure 11* that while the rate of bond scission increases with acrylonitrile content it does not increase nearly in proportion. In addition, the numbers of monomer
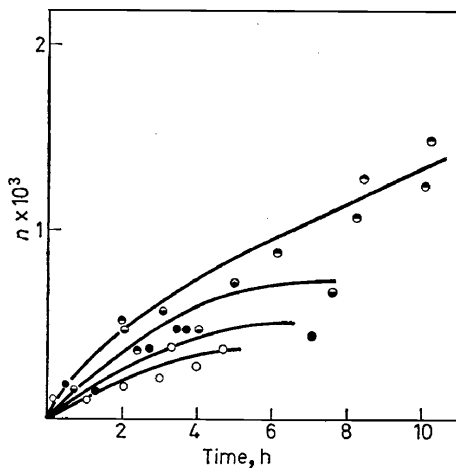

Figure 11. Chain scissions in methyl methacrylate/acrylonitrile copolymers as a function of time of photo-degradation at 160°C (○, 410/1; ●, 40/1; ◓, 16/1; ◑, 8/1)

molecules produced per scission of the 410/1, 40/1, 16/1 and 8/1 copolymers are 1710, 728, 512 and 256 respectively, whereas one would expect maximum values of 820, 80, 32 and 16 if the reaction consisted only of depolymerization to the next acrylonitrile unit after each chain scission. Bearing in mind that the polymer at 160° is in the form of a highly viscous liquid, these observations have been accounted for in the following way. Once the broken ends have depolymerized to acrylonitrile units, the resulting acrylonitrile terminated radicals are virtually trapped and the closer they are together, that is the richer the copolymer is in acrylontrile, the greater will be the probability that recombination of the broken ends will occur. Thus, in the 8/1 copolymer in particular the effect will be that few of the original scissions are permanent. In copolymers containing progressively less acrylonitrile, the effect of depolymerization will be to bring the radicals further from each other and thus to make the probability of recombination progressively less. These are the essential facts although there is a great deal of additional information in support of these mechanisms for the thermal and photo-reactions.

It is clear that if e.s.r. measurements could be made during these two degradation processes it is possible that they might supply the ultimate proof that these deductions, made principally on the basis of rate and molecular-weight measurements, are correct or, alternatively, that they must be modified. In the thermal reaction, for example, one would expect to obtain an e.s.r. spectrum typical of the methyl methacrylate radical. It might be the nine-line spectrum already discussed and which is composed of overlapping four- and five-line spectra or possibly a simpler six-line spectrum due to the five β protons becoming equivalent as a result of the greater mobility of the methyl and methylene groups in the relatively much less viscous polymer at the higher temperature of the thermal reaction. In either case, the spectrum would be expected to be fundamentally different from that obtained during the photo-initiated reaction which should reflect a higher concentration of acrylonitrile type radicals,

$$\sim\!\!\sim\!\!CH_2\!-\!\!\overset{\displaystyle CN}{\underset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}\cdot$$
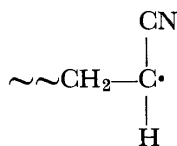
This spectrum will probably be rather complicated. Ideally, interaction with the nitrogen atom should be expected to give three lines of equal intensity. These might be split into triplets by interactions with the methylene protons, each line of which might be further split into a doublet by interaction with the α proton, giving 18 lines in all.

If the experimental difficulties can be overcome such that e.s.r. spectroscopy can be applied to the solution of problems of this kind, then within the next few years, this technique could become one of the most vitally important in allowing rapid new advances to be made in our understanding of polymer degradation processes.

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