PHOTODEGRADATION OF METHACRYLATE/ACRYLATE COPOLYMERS

N. GRASSIE

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

ABSTRACT

Although the effects of u.v. radiation on poly(methyl methacrylate) and poly-(methyl acrylate) are superficially different, nevertheless there are obvious fundamental similarities and this copolymer system was chosen for study in order to observe the influence of one type of chain unit on the degradation reactions of the other. Rates of chain scission and crosslinking were measured at room temperature on copolymer films covering the whole composition range using molecular weight and sol gel analysis measurements. Crosslinking is associated with sequences of two or more methyl acrylate units but chain scission passes through a minimum at a methyl methacrylate content in the region of 40 to 50 per cent.

Crosslinking is inhibited in solution and differences in the relationship between chain scission and composition compared with degradation in film can be accounted for in terms of the relative mobilities in film and solution of the primarily formed radicals. The environment in which these radicals find themselves has also a strong influence on the pattern of volatile degradation products.

Relationships between these reactions and the thermal and photothermal degradation which occurs in acrylate/methacrylate systems are described and discussed.

The various contributions to this symposium have demonstrated the diversity of interest which exists in the interaction of visible and ultra-violet radiation with polymeric systems. It has also been recognized, almost since polymers first became commercially significant, that their resistance to this type of radiation is a very large factor in determining their useful life. Thus the commercial importance of the degradative effects of radiation and the comparatively more recent interest in the more fundamental interaction of radiation with matter have together stimulated interest in the photodegradation of polymers especially during the past five to ten years.

During this period a great deal of progress has been made in understanding the mechanism of photodegradation of a number of homopolymers and the position in 1967 was admirably reviewed by Dr Fox[1] who is contributing to this symposium in other directions. Since that time significant contributions have been made, particularly in Belgium by Dr Geuskens, Dr David and their collaborators[2–4].

In my laboratory during the past few years we have attempted to contribute to a more fundamental understanding of photodegradation processes by

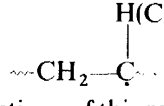
studying the effects of a number of experimental variables and the following are some of the topics which have been of particular interest to us:

(a) A comparison of the reactions which occur in polymer films and solutions.
(b) A comparison of the reactions which occur in copolymers with those which are characteristic of the two homopolymers.
(c) The effect of crystallinity on the rate of degradation.
(d) The relative rates of degradation above and below the glass transition temperature.
(e) The influence of radiation on the subsequent thermal degradation properties of the polymer.
(f) A comparison of the photolysis reactions which occur in molten polymers (photothermal degradation) with the purely thermal reactions which occur at slightly higher temperatures.

In this lecture I shall describe a few observations which we have made in some of these directions. Because of the limited time at my disposal I shall confine my remarks to observations on copolymers of methacrylates and acrylates. I should like you to regard it as a progress report which as yet only provides a few of the definitive answers to the problems we have set ourselves to solve.

Although polymethacrylates and polyacrylates are so similar structurally it has been known for a long time that many of their degradation characteristics and products are quite different. Degradation reactions in their copolymers are therefore particularly interesting because they demonstrate how two monomers with different degradation tendencies can interact on one another when they find themselves in the same degrading polymer molecule.

Under u.v. radiation at ordinary temperatures, poly(methyl methacrylate) undergoes chain scission, the molecular weight decreasing rapidly, while poly(methyl acrylate) becomes insoluble due to crosslinking of the polymer molecules. Looking more closely at these reactions, however, it is clear that they also have a great deal in common because the gaseous products of reaction, although they are produced in relatively small quantities, are identical[1]. These are principally methyl formate, methanol, methane, hydrogen, carbon monoxide and carbon dioxide formed by decomposition of the ester side group. Thus it seems clear that the primary effect of u.v. radiation is to cause scission of the ester side group giving the radical



and that the subsequent reactions of this radical determine the more obvious changes which occur. Thus polymethacrylate radicals predominantly undergo chain scission while acrylate radicals predominantly combine. Our immediate interest was to study copolymers of these two monomers so that the interaction of one type of chain unit on the degradation reactions of the other might be observed.

Thin films of copolymers covering the whole composition range were irradiated under a fixed intensity of 2537 Å radiation for various times.

Only those copolymers containing more than 50 mole per cent methyl methacrylate remain soluble. For these, rates of chain scission were calculated from the change in molecular weight using the formula,

$$N = 1/CL_t - 1/CL_0 \quad (1)$$

in which N is the number of scissions per monomer unit and CL_0 and CL_t are the number average chain lengths at zero time and time t. Copolymers containing $\leqslant 50$ mole per cent of methyl methacrylate become progressively

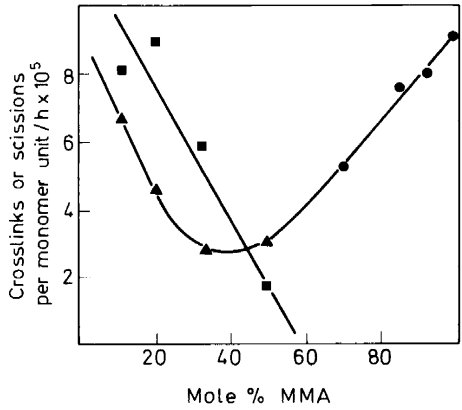


Figure 1. Dependence of rates of scission and crosslinking on the composition of MMA/MA copolymers irradiated in the form of films. ●, chain scission (equation 1); ▲, chain scission (equation 2); ■, crosslinking (equation 2).

insoluble during irradiation. Sol–gel analyses were carried out on these and the data analysed using the Charlesby–Pinner equation[5].

$$S + \sqrt{S} = p_0/q_0 + 1/q_0ut \quad (2)$$

in which S is the sol fraction, p_0 and q_0 are rates of scission and crosslinking, u is the number average degree of polymerization of the starting material and t is the time of irradiation. The data obtained are illustrated in *Figure 1*.

A number of interesting facts are revealed by the data in *Figure 1*. First, although the rate of crosslinking decreases with the decreasing acrylate content of the copolymer as expected, an extrapolation suggests that it is effectively zero even in copolymers containing as much as 45 mole per cent of methyl acrylate. Thus crosslinking is not to be associated with single methyl acrylate units in the copolymers but with sequences of two or more. Secondly, the shape of the chain scission curve is perhaps unexpected. Certainly one might reasonably expect the rate of chain scission to decrease with decreasing methyl methacrylate content at high methacrylate contents but the minimum in the vicinity of 40 to 50 per cent methyl methacrylate and the subsequent rapid increase so that the rate of scission in pure poly(methyl acrylate) is seen to be of the same order as that in pure poly(methyl methacrylate) is surprising.

Further insight into the chemical nature of the chain scission process in poly(methyl methacrylate) films is provided by the observation that thermal instability develops as a result of u.v. irradiation[6]. This has been convincingly

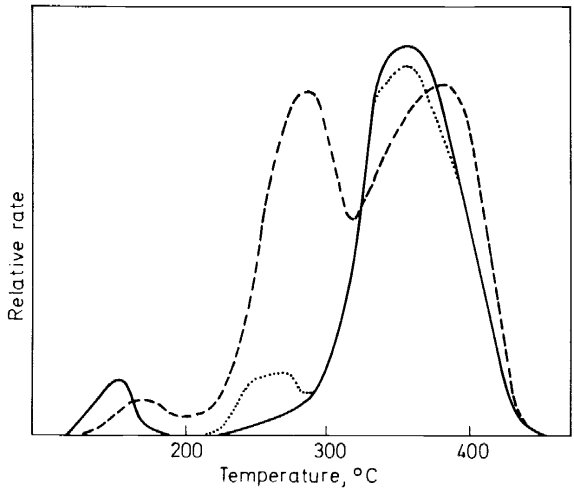
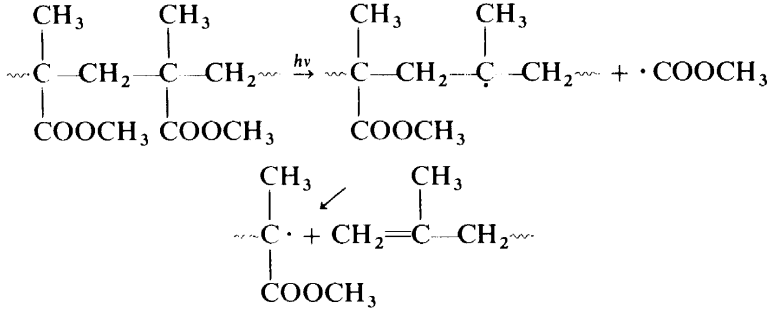


Figure 2. TVA thermograms for poly(methyl methacrylates). ——, anionic; – – –, free radical; · · · · · ·, anionic after irradiation.

illustrated by McNeill[7] using the technique of Thermal Volatilization Analysis (TVA). This technique measures continuously the rate of volatilization of a polymer sample as the temperature is raised. TVA thermograms of typical radical and anionically initiated poly(methyl methacrylates) are illustrated in *Figure 2*. The main peaks in each thermogram are due to liberation of monomers by depropagation or 'unzipping' of the radicals formed by random scission of the polymer molecules. However, radical initiated polymer, but not anionic polymer, incorporates a proportion of unsaturated terminal structures formed in the disproportionation termination reaction and the low temperature peak in the thermogram of the radical polymer is due to initiation of the degradation reaction at these labile structures. The thermogram of pre-irradiated anionic polymer, also illustrated in *Figure 2*, demonstrates that similarly labile structures have been formed, probably in the sequence



The study of degradation reactions in polymer films which I have been describing is obviously closely relevant to the commercial application of polymers because, in their major applications, polymers are used in the solid state rather than as liquids or in solution. However, the solid phase has a

number of important disadvantages when more fundamental kinetic and mechanistic studies are to be made as a step towards a more complete understanding of the chemical changes which are occurring. For example, in the solid phase one cannot observe the effect on the reaction of a change in the concentration of the polymer. In solution it is also easier to study the kinetic effects of additive materials such as stabilizers, radiation absorbents, antioxidants and other types of inhibitors. If the study of reactions in solution is to contribute to our understanding of reactions in the solid phase it is important, of course, that the main characteristics of the reaction in the two phases should be similar. Yet minor differences in behaviour may contribute to a more complete understanding if the reasons for them can be clarified.

In solution, u.v. radiation does not cause insolubility in poly(methyl acrylate) or methyl acrylate rich copolymers with methyl methacrylate as it does in film. It may be assumed that this is because crosslinking is inhibited in solution by the separation of the polymer molecules by molecules of the solvent. Equation 1 may thus be applied to molecular weight measurements made during irradiation of copolymers in solution in methyl acetate leading to the data in *Figure 3*. The close similarity between the principal characteristics of the photodegradation of methyl methacrylate/methyl acrylate copolymers in the solid phase and in solution is demonstrated by comparison of *Figures 1 and 3*. The intensity of irradiation in each case was comparable.

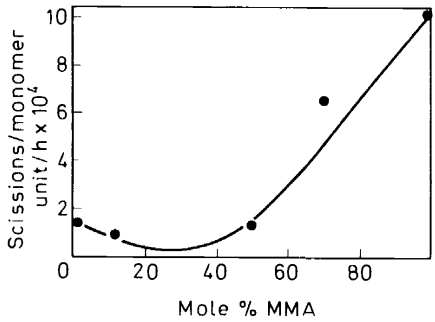


Figure 3. Dependence of rates of scission on the composition of MMA/MA copolymers irradiated in solution in methyl acetate.

A closer comparison of *Figures 1* and *3* reveals that while the rates of chain scission in poly(methyl acrylate) and methyl acrylate rich copolymers in film and in solution are comparable, the rate of chain scission in methyl methacrylate rich copolymers is very much greater in solution. The possibility that crosslinking is occurring at the methyl acrylate end of the composition range and thus depressing that end of the curve in *Figure 3* was investigated by measuring the rate of chain scission in varying concentrations of pure poly(methyl acrylate). The result is shown in *Figure 4*. Since the rate does not change with polymer concentration and since the solution rate, measured using equation 1, is identical with the rate in film, measured using equation 2, it may reasonably be concluded that both methods of measuring chain scission are reliable, that crosslinking is eliminated in solution and

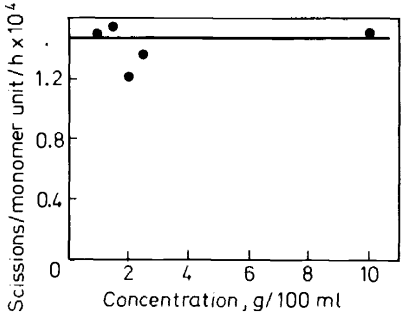


Figure 4. Effect of concentration on the rate of chain scission induced by u.v. radiation in poly(methyl acrylate).

that the enhanced rate in solution at the methyl methacrylate end of the composition range is a genuine effect which must be explained in any comprehensive account of the reaction mechanism.

One obvious difference between the methyl acrylate and methyl methacrylate ends of the copolymer composition range is that the glass transition temperatures of high methyl acrylate copolymers are below the ordinary temperatures at which these film and solution photolyses were carried out while the glass transition temperatures of high methacrylate copolymers lie well above ambient temperatures. The values of T_g for poly(methyl methacrylate) and poly(methyl acrylate) are 105°C and 6°C respectively[8]. It might thus reasonably be predicted that the immobility of the polymer molecules in high methacrylate copolymers would result in a high proportion of 'cage' recombination of the primary radical products. In solution, on the other hand, these primary radicals would more readily diffuse apart thus explaining the higher rate of degradation in solution. Because, at ordinary temperatures, high acrylate copolymers are above their glass transition temperatures there would be much less tendency to 'cage' recombination of radicals and rates

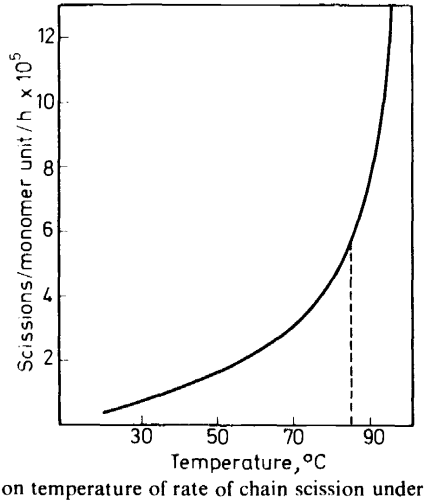


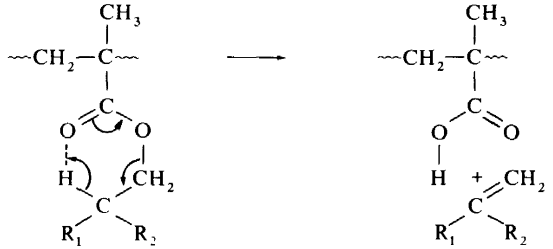
Figure 5. Dependence on temperature of rate of chain scission under u.v. radiation of a 70/30, MMA/MA copolymer.

of degradation in film would increase towards the rates in solution.

In order to test this theory some preliminary experiments have been carried out in which the rates of photolytic scission of a high methacrylate copolymer have been measured over a range of temperatures above and below the glass transition point. The glass transition temperature, measured by DTA, is 82°C and *Figure 5* illustrates the rapid increase in the rate of photolytic scission which occurs in the vicinity of this temperature.

But there are also fundamental differences in the nature of the volatile degradation products when methacrylate/acrylate copolymers are irradiated below and above the glass transition temperature. The photolysis reactions which occur in molten polymers at temperatures just below the threshold of thermal degradation have been referred to as photothermal degradations because interesting comparisons may often be made between them and the purely thermal processes which occur at slightly higher temperatures.

In the thermal degradation of polymethacrylates, which begins at approximately 200°C, there are two principal competing reactions, namely, depolymerization to monomer and ester decomposition in which the olefin corresponding to the ester group is liberated as a volatile product and poly(methacrylic acid) residues remain in the polymer molecules. The latter usually proceeds by a molecular mechanism which depends upon interaction between the carbonyl group and β hydrogen atoms



and the data in *Table 1* demonstrate how this reaction is favoured by high concentrations of β hydrogen atoms in the monomer structure.

However, under photothermal conditions, say at 160°C, radicals are produced by the radiation at temperatures lower than that at which thermal degradation occurs and almost quantitative yields of monomer are obtained from all the methacrylates including the *t*-butyl ester in which ester decomposition occurs almost exclusively under purely thermal degradation conditions.

This difference between the products of photodegradation in film and

Table 1. Influence of β hydrogen atoms on the mechanism of degradation of polymethacrylates

Depolymerization		Mainly depolymerization		Ester decomposition	
Methyl	0	Ethyl	3	(Ethyl)	2
neo-Pentyl	0	*n*-Propyl	2	iso-Propyl	6
iso-Butyl	1	*n*-Butyl	2	sec-Butyl	5
Ethoxyethyl	2	*n*-Hexyl	2	tert-Butyl	9
		n-Heptyl	2		
		n-Octyl	2		

solution on the one hand and of photothermal degradation on the other can be explained in terms of the equilibrium which exists between propagation and depropagation,

$$M_n^{\cdot} \rightleftarrows M_{n-1}^{\cdot} + M$$

in which $M_n^{\cdot}$ and $M_{n-1}^{\cdot}$ are polymer radicals, n and $n-1$ monomer units in length, and M is a monomer molecule. At higher temperatures in molten polymer, conditions are such that monomer is continuously removed so that the equilibrium tends to the right and high yields of monomer are obtained. In film at ambient temperature, monomer cannot freely escape so that each radical will find itself effectively surrounded by a high concentration of monomer and the monomer-producing reaction is inhibited. In solution the equilibrium concentration of monomer, which is quite low, will be rapidly built up because solution experiments are invariably carried out in a closed system because of the volatility of the solvent. It would be interesting in this connection to carry out photolysis in solution in an involatile solvent so that monomer could be continuously removed.

Although little work has been reported on the photothermal degradation of polyacrylates it seems that crosslinking predominates as in solid film. In methacrylate/acrylate copolymers[9] an interesting new situation arises because unzipping, initiated in the methacrylate segments of the molecules, cannot pass freely through acrylate units to liberate high yields of acrylate monomer. Instead, quite different types of acrylate decomposition reactions occur. In order to be able to distinguish acrylate decomposition products more readily from methacrylate decomposition products, it has been found convenient in this phase of the work to extend earlier studies of the methyl methacrylate/methyl acrylate copolymer system[9] to copolymers of methyl methacrylate and *n*-butyl acrylate.

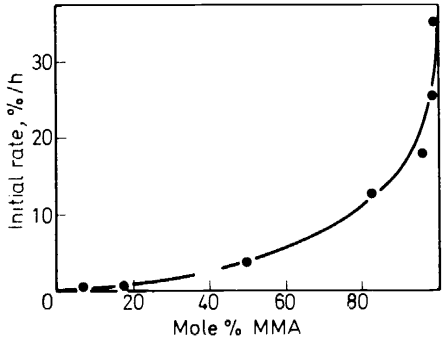


Figure 6. Rates of volatilization of methyl methacrylate/*n*-butyl acrylate copolymers degrading under photothermal conditions at 165°C.

The strong inhibiting effect of *n*-butyl acrylate on the unzipping reaction in poly(methyl methacrylate) is illustrated by the data in *Figure 6*. This figure demonstrates that rates of volatilization only become appreciable when the methacrylate content of the copolymer is greater than 50 per cent, suggesting that although the depropagation process can pass through single acrylate units, it is very much more efficiently inhibited when significant

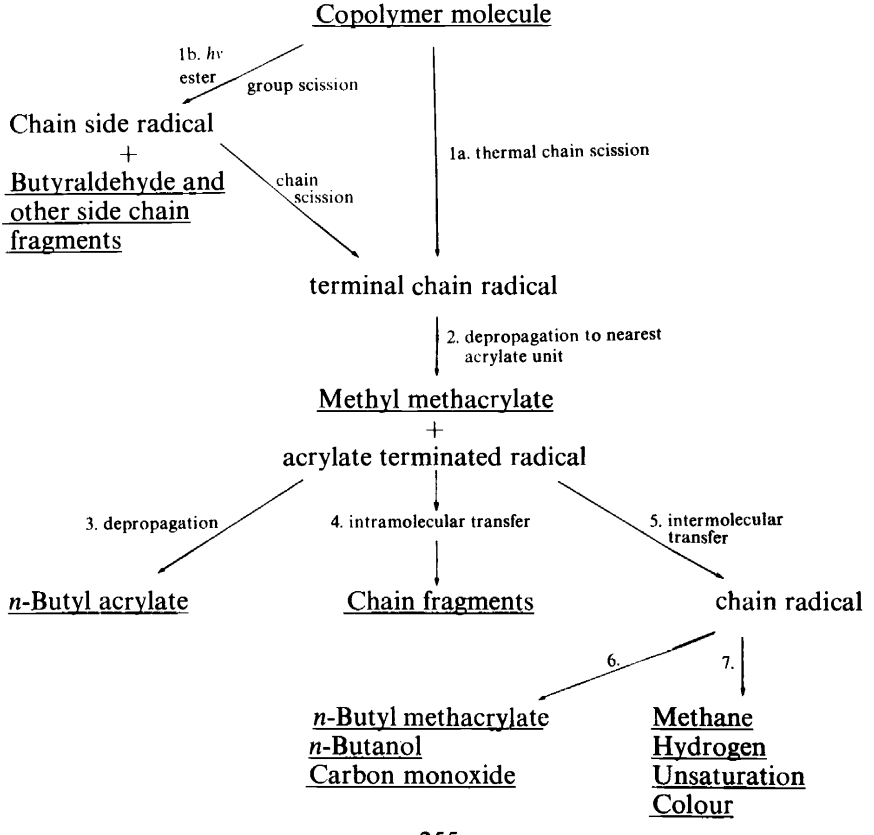
concentrations of sequences of two or more acrylate units occur in the polymer molecule.

The principal products of the photothermal degradation of copolymers of methyl methacrylate and *n*-butyl acrylate are listed in *Table 2*.

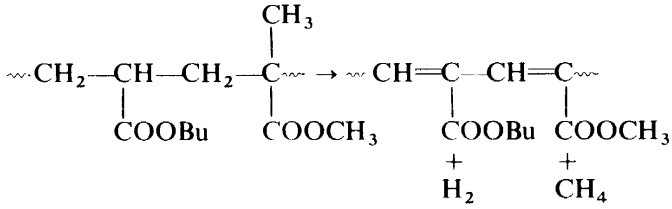
Table 2. Products of photothermal degradation of copolymers of methyl methacrylate and *n*-butyl acrylate

Methyl methacrylate	chain fragments
n-Butyl acrylate	hydrogen
n-Butyl methacrylate	methane
n-Butyraldehyde	carbon monoxide
n-Butanol	conjugated unsaturation

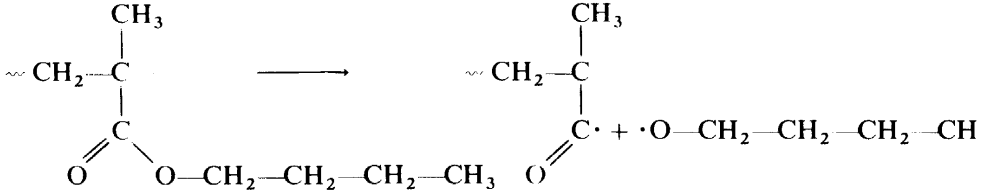
These are identical with the products of the purely thermal degradation reaction except that butyraldehyde, which is an important product of the photothermal reaction, is completely absent in the thermal reaction. It seems that the thermal and photothermal reactions are identical apart from the initiation process which is main chain scission in the thermal reaction but is associated with the decomposition of the ester side chain in the photothermal reaction. The products are accounted for by the following reaction sequence.

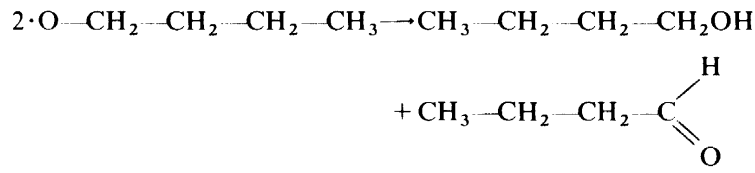


After radical formation either thermally or photolytically (1a) or (1b), depropagation (2) occurs in methyl methacrylate sequences as far as the first *n*-butyl acrylate unit. The main pattern of products then depends upon the subsequent reactions of the *n*-butyl acrylate terminated radical. There is a small tendency to depropagation (3) to form *n*-butyl acrylate monomer. Alternatively the radical may abstract a hydrogen atom farther along its own chain in an intramolecular transfer process (4). Scission at this point would result in a chain fragment and a new chain terminal radical. On the other hand, transfer to another chain in an intermolecular transfer reaction (5) would result primarily in a chain radical of the type believed to be primarily formed by u.v. radiation. It is believed that this radical may undergo a number of complex reactions (6) to produce *n*-butyl methacrylate, *n*-butanol and carbon monoxide and that a further reaction (7) is initiated which is closely akin to the reaction which results in the liberation of hydrogen chloride from poly(vinyl chloride) leaving a conjugated, coloured residue. In this way it is believed that hydrogen and methane are liberated from acrylate and methacrylate units respectively and the residual material incorporates conjugated unsaturation.



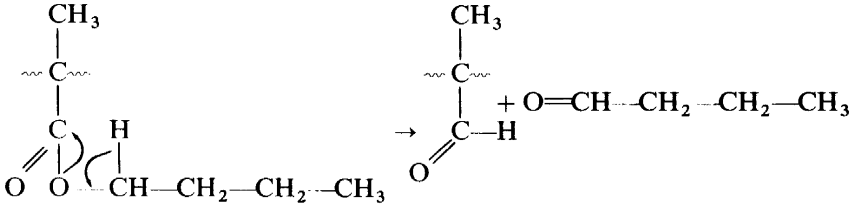
The butyraldehyde, formed only in the photoinitiation process could be accounted for by alkyl oxygen scission followed by disproportionation of pairs of alkoxy radicals.





This would imply the formation of equimolar amounts of the alcohol and aldehyde. However, while the butyraldehyde yield is roughly proportional to the butyl acrylate content of the copolymer, butyl alcohol is only produced

from copolymers containing more than 50 mole per cent of butyl acrylate. An alternative explanation is direct splitting out of butyraldehyde following activation of the neighbouring bonds by the radiation absorbed by the carbonyl chromophore.



A high proportion of the data which I have described in this lecture are as yet unpublished. For this reason I will conclude by gratefully acknowledging the contributions made by my colleagues Dr Duncan Fortune, Dr Roy Jenkins, Dr Alan Scotney and Dr Irwin Davis.

REFERENCES

[1] R. B. Fox, *Progress in Polymer Science*, Vol. I, A. D. Jenkins (Ed.). Pergamon, London (1967).
[2] C. David, W. Demarteau and G. Geuskens, *Polymer, London*, **8**, 497 (1967).
[3] C. David, W. Demarteau, F. Derom and G. Geuskens, *Polymer, London*, **11**, 61 (1970).
[4] C. David, W. Demarteau and G. Geuskens, *Polymer, London*, **10**, 21 (1969).
[5] A. Charlesby and S. H. Pinner, *Proc. Roy. Soc. A*, **249**, 367 (1959).
[6] C. David, D. Fuld, G. Geuskens and A. Charlesby, *Europ. Polym. J.* **5**, 641 (1969).
[7] I. C. McNeill and D. Neil, *Thermal Analysis*, p 353. R. F. Schwenker and P. D. Garn (Eds.). Academic Press: New York (1969).
[8] *Polymer Handbook*, Brandrup and Immergut (Eds.). Interscience: New York (1966).
[9] N. Grassie, B. J. D. Torrance and J. B. Colford, *J. Polym. Sci. A-1*, **7**, 1425 (1969).