Relationships between Thermal, Photothermal and Photolytic Degradation Processes in Methacrylate/Acrylate Copolymers*

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Degradation reactions in acrylate/methacrylate copolymers have been studied under four sets of conditions, namely, photolysis reactions in film and in solution at ordinary temperatures, photothermal reactions, that is photolysis reactions in molten polymer below the thermal degradation threshold, and thermal degradations. The paper seeks to demonstrate some of the relationships which exist between these reactions.

Methyl methacrylate (MMA)/methyl acrylate (MA) copolymer films have been irradiated with 2537 Å radiation and the rates of scission and crosslinking obtained from molecular weight measurements and sol-gel analysis. Crosslinking decreases with methyl acrylate content to zero when 45 mole % of acrylate is present in the copolymer. It is concluded that crosslinking is associated with groups of adjacent methyl acrylate units rather than single units. Rates of chain scission are comparable in pure poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) but pass through a minimum at 40 mole % MMA.

Crosslinking is inhibited in solution. The rate of chain scission again passes through a minimum at $30-40\%$ MMA in the copolymer and although PMA scissions at comparable rates in film and in solution, the rate of scission of PMMA is greatly accelerated in solution.

Under photothermal degradation conditions $(160-170°C)$ the primarily formed methacrylate radicals can unzip to form monomer but in copolymers, unzipping is inhibited by acrylate units and a new series of acrylate decomposition products appears including (from a butyl acrylate copolymer) n-butyl methacrylate, n-butyraldehyde and n-butanol. These and other products have been accounted for qualitatively.

At the higher temperature at which thermal degradation occurs (220°C) a similar spectrum of products appears to that in the photothermal reaction but the higher temperature often induces new kinds of reactions which may yield new products and also interfere with, and thus modify, the radical reactions and thus the products typical of photothermolysis. Examples are discussed.

Thermal and photolytic degradation reactions in polymers are usually regarded as being quite different from one another. Yet the kinds of reactions which may be induced by heat or u.v. radiation, although superficially different, can have many features in common. In recent years this has been demonstrated by various kinds of degradation studies on acrylate and methacrylate homopolymers and copolymers [1—5] and it is being found that the results of these investigations are now uniting into a single unified picture.

Although polyacrylates and polymethacrylates 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 the 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.

Degradation reactions carried out under four conditions have been studied as follows:

1. Photolysis of polymer films at ordinary temperatures [6].

2. Photolysis of polymers in solution at ordinary temperatures [7].

3. Photothermal degradations, that is, photolysis of polymers above their melting points but below the thermal degradation threshold [2, 8].

4. Thermal degradation [3, 4].

The purpose of this paper is to demonstrate, by means of suitable examples, some of the relationships which exist between these degradation processes in acrylate and methacrylate homopolymers and copolymers, and to show that it can be profitable to study these four kinds of reactions in conjunction with one another.

Photolysis of polymer films

It is now quite generally accepted that the effects of u.v. irradiation of methacrylate and acrylate homopolymers are superficially quite different [5]. Poly(methyl methacrylate), for example, undergoes chain scission, the molecular weight decreasing rapidly, while poly(methyl acrylate) becomes rapidly 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 produced in relatively small quantities, are identical in each case [9—12]. They 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,

$$\sim -CH_2 - \overset{\overset{\displaystyle H(CH_3)}{\displaystyle |}}{\underset{\displaystyle \cdot}{C}} - \sim$$
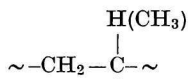
and that the subsequent reactions of this radical determine the more obvious changes which occur. Thus polymethacrylate radicals predominantly undergo main chain scission while acrylate radicals predominantly combine. Because the behaviours of the two homopolymers are so different it is of interest to study the behaviours of their copolymers so that the interaction of one type of chain unit on the degradation reactions of the other may be observed.

Thin films of a series of copolymers of methyl methacrylate and methyl acrylate have been irradiated under a fixed intensity of 2537 Å radiation [6]. Those copolymers containing more than 50 mole % of methacrylate remain soluble. The rates of chain scission were calculated from the change in molecular weight using the formula,

$$N = \frac{1}{CL_t} - \frac{1}{CL_0} \qquad (1)$$

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 50 mole % or less of methyl methacrylate become progressively insoluble during irradiation. Sol-gel analyses were carried out and the data analysed using the Charlesby—Pinner equation [13]

$$s + \sqrt{s} = p_0/q_0 + 1/q_0\, ut \qquad (2)$$

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 polymerisation of the starting material and t is the time of irradiation. In this way rates of chain scission and crosslinking were derived. All of these data are illustrated in Fig. 1.

A number of interesting facts are revealed by the data in Fig. 1. Firstly, 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 % of methyl acrylate. Thus crosslinking is not to be associated with single methyl acrylate units 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—50% 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.
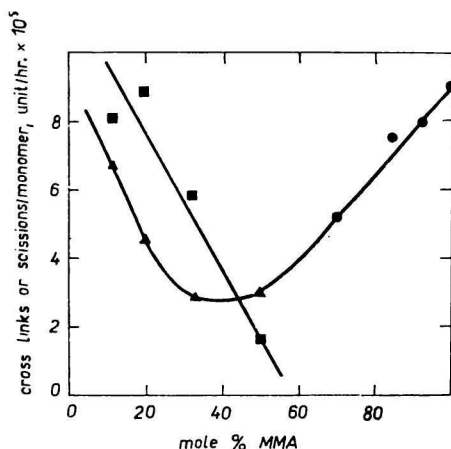

Fig. 1. Dependence of rates of scission and crosslinking on the composition of MMA/MA copolymers irradiated in the form of film. ● chain scission (equation 1); ▲ chain scission (equation 2); ■ crosslinking (equation 2).
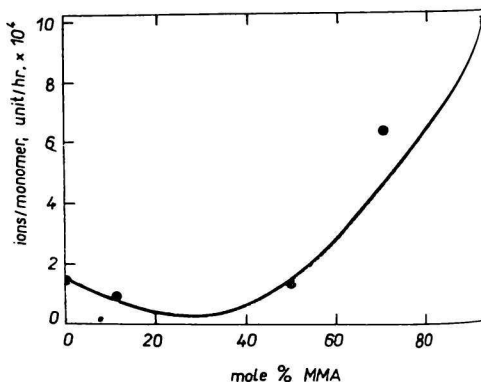
Fig. 2. Dependence of rates of scission on the composition of methyl methacrylate/methyl acrylate copolymers irradiated in solution in methyl acetate.

These experiments show that the decrease in molecular weight which occurs in poly-(methyl methacrylate) and the insolubilisation which occurs in poly(methyl acrylate) are not simply the result of chain scission and crosslinking processes at isolated methyl methacrylate and methyl acrylate units. The mechanisms of these reactions are obviously much more complicated than this and will be discussed in subsequent papers [6].

Photolysis of polymers in solution

The study of degradation reactions in polymer films, to which the previous section of this paper was devoted, 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 stabilisers, 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 [7]. If it is assumed that this is because crosslinking is inhibited in solution by the separation of the polymer molecules by molecules of the solvent then the application of equation *1* to molecular weight measurements made during irradiation of copolymers in solution in methyl acetate leads to the data in Fig. 2. 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 Figs. 1 and 2. The intensity of irradiation in each case was comparable.

A closer comparison of Figs. 1 and 2 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 Fig. 2 was investigated by measuring the rate of chain scission in varying concentrations of pure poly(methyl acrylate). The result is shown in Fig. 3. 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 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.

Photothermal degradation

When methacrylate/acrylate copolymers are subjected to u.v. irradiation in the molten state at temperatures below the thermal degradation threshold, the degradation charac-

teristics are quite different from those observed in the solid state or in solution at lower temperatures.

It is a general property of the methacrylate homopolymers that they decompose quantitatively to monomer under these conditions. The methyl, ethyl, n-butyl and tert-butyl esters certainly do so. It seems that radicals are formed by elimination of the ester group and that this is followed, as at low temperatures, by chain scission. The radicals thus formed are able to depropagate or unzip to give high yields of monomer under these molten polymer conditions.
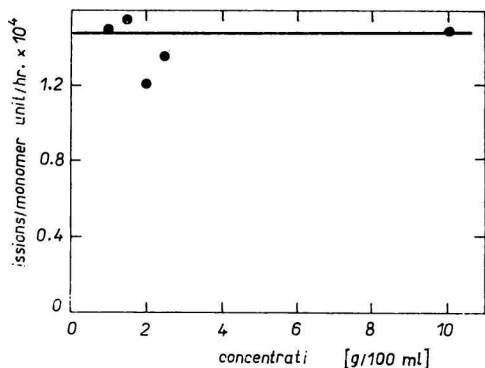
Fig. 3. Effect of concentration on the rate of chain scission induced by u.v. radiation in poly(methyl acrylate).
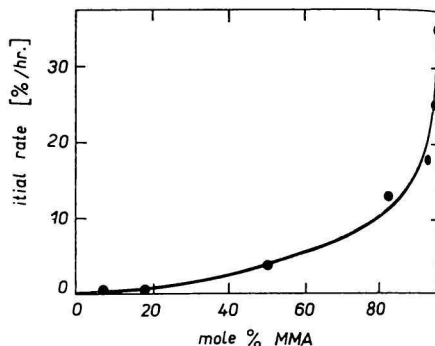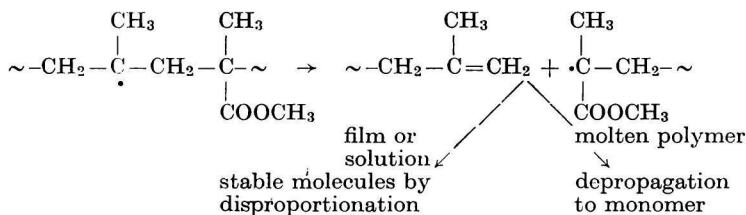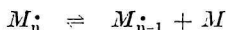
Fig. 4. Rates of volatilisation of methyl methacrylate/n-butyl acrylate copolymers degrading under photothermal conditions at 165°C.

This difference in behaviour can be most satisfactorily explained in terms of the equilibrium which exists between propagation and depropagation and which may be represented as follows,

$$M_n^{\bullet} \;\rightleftharpoons\; M_{n-1}^{\bullet} + M$$

in which $M_n^{\bullet}$ and $M_{n-1}^{\bullet}$ are polymer radicals, n and n-1 monomer units in length and M is a monomer molecule. At high 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. The equilibrium concentration of monomer, which is quite low, will be rapidly built up in solution because

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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 poly-acrylates it seems that crosslinking predominates [8] as in solid film. In methacrylate/ /acrylate copolymers [2, 8] 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 [2] to copolymers of methyl methacrylate and n-butyl acrylate [8].

The strong inhibiting effect of n-butyl acrylate on the unzipping reaction in poly-(methyl methacrylate) is illustrated by the data in Fig. 4. This figure also demonstrates that rates of volatilisation only become appreciable when the methacrylate content of the copolymer is greater than 50%, 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 1.

The relative amounts of the various products vary with copolymer composition, the highest monomer yields being obtained from methyl methacrylate rich copolymers. These products may be accounted for in a qualitative way by the following reaction sequence.

Copolymer molecule

1. ↓ chain scission

terminal chain radical

2. ↓ depropagation to
nearest acrylate unit

methyl methacrylate

+

acrylate terminated radical

3. depropagation	*4.* intramolecular transfer	*5.* intermolecular transfer
↓	↓	↓
n-butyl acrylate	*chain fragments*	chain radical

6. n-butyl methacrylate *7. methane*
  n-butanol   *hydrogen*
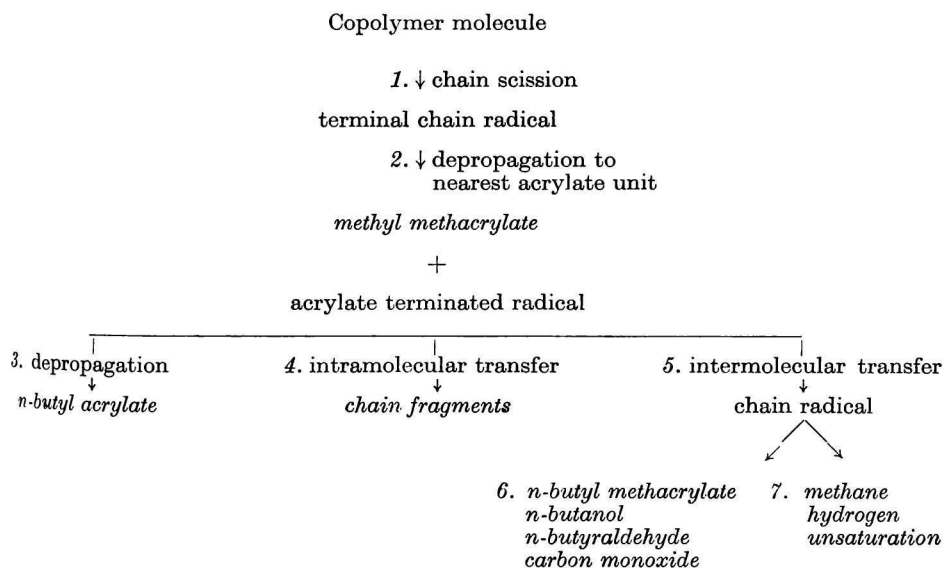 *n-butyraldehyde*   *unsaturation*
  carbon monoxide

Table 1

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

Table 2

Products of thermal and photothermal degradation of polymethacrylates

Polymethacrylate	Photothermal	Thermal
methyl	monomer in high yield	monomer in high yield
n-butyl [14]	monomer in high yield	monomer in intermediate yield; trace of butene
tert-butyl [15]	monomer in high yield	isobutene in high yield; trace of monomer

After chain scission (*1*) of the type discussed above, 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 further 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, *n*-butyraldehyde 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

$$\sim -CH_2-CH-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\sim \quad \rightarrow \quad \sim -CH=\underset{\underset{COOBu}{|}}{C}-CH=\underset{\underset{COOCH_3}{|}}{C}-\sim$$

$$+ \qquad +$$
$$H_2 \qquad CH_4$$

where the left structure has COOBu below the CH.
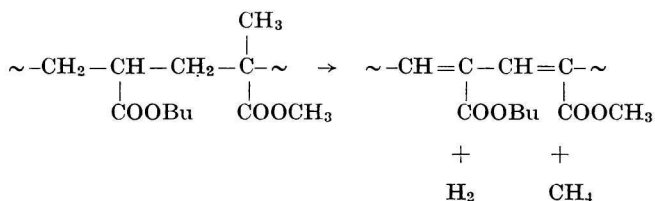
The detailed mechanisms of these reactions have been discussed elsewhere [1—10]. From the point of view of this present paper it is important to emphasise the fact that all the products can be accounted for in terms of a single concerted mechanism.

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Thermal degradation

Photothermal reactions in acrylate—methacrylate systems have commonly been carried out at temperatures in the vicinity of 170°C. This temperature has been chosen because it is well above the melting point of this class of materials and yet well below their thermal degradation threshold, which is approximately 200°C. Above 200°C homolytic scission of the most thermally labile bonds must occur because thermal reactions in these systems are often predominantly radical reactions yielding the same spectrum of products as photothermally induced reactions although perhaps in different proportions But the slightly higher temperature required for thermal degradation is often sufficient to induce new kinds of reactions which may superimpose new products on those of the photothermal reaction or even interfere with the radical mechanism so that it is inhibited such that only the new products appear.

A simple example of this behaviour is provided by the homopolymers of methyl, *n*-butyl [14] and *tert*-butyl [15] methacrylates. Their photothermal and thermal degradation behaviours are presented in Table 2.

Photothermal degradation of all three esters results in almost quantitative yields of monomer. In the methyl ester, photothermal and thermal mechanisms are almost identical. In the thermal degradation of the *tert*-butyl ester, the simple unzipping process is quickly blocked by the products, namely acid or anhydride, of an ester decomposition reaction which only becomes possible at the higher temperature of the thermal reaction.
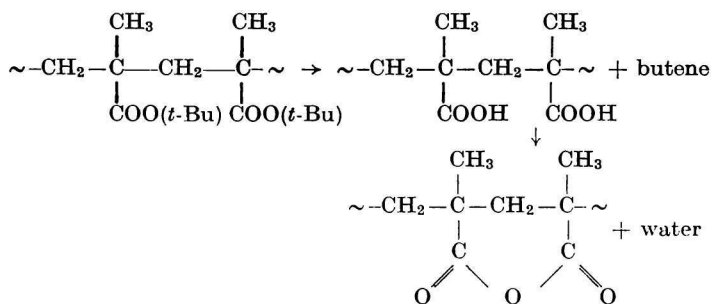
The thermal degradation behaviour of the *n*-butyl ester represents an intermediate situation in which a relatively small proportion of ester decomposition occurs but which is sufficient to have a profound effect on monomer production.

In the thermal degradation of acrylate/methacrylate copolymers [1, 4] these ester decomposition products are superimposed on the already complex mixture of products revealed in photothermal degradation.

It is the existence of these kinds of relationships between thermal, photothermal and photolysis reactions in film and in solution which has made it profitable to study all four kinds of reactions in parallel with each other in this laboratory over the past few years.

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