

RECENT WORK ON THE THERMAL DEGRADATION OF ACRYLATE AND METHACRYLATE HOMOPOLYMERS AND COPOLYMERS

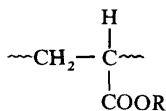
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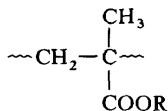
ABSTRACT

The principal degradation reactions which occur in polymethacrylates are depolymerization to monomer and ester decomposition yielding methacrylic acid units in the polymer and liberating the corresponding olefin. The greater the number of β hydrogen atoms in the ester group the greater the tendency towards ester decomposition. There is also a strong tendency to ester decomposition in polyacrylates incorporating large numbers of β hydrogen atoms but the degradation processes which occur in primary esters are much more complex. The mechanisms of all these reactions are discussed. The behaviour of acrylate-methacrylate copolymers throws further light on these basic processes. In the light of an accumulation of experimental results an integrated mechanism for the thermal degradation of homopolymers and copolymers of acrylates and methacrylates is presented.

It has for long been recognized that the principal products of the thermal degradation of polyacrylates (I) and polymethacrylates (II) are quite different from each other in spite of the close structural similarities between the two



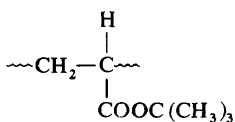
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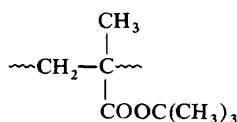
(II)

families of polymers. On the one hand, large yields of monomer are obtained from many methacrylates, while, on the other, most acrylates give high yields of a mixture of chain fragments several monomer units in length.

However, analyses of minor products of reaction demonstrate that the degradation reactions in the two classes of polymers also have many similarities and the degradation mechanisms obviously coincide in the two tert-butyl esters^{1, 2} (III) and (IV) from both of which almost quantitative yields of isobutene are evolved without either monomer or chain fragments.



(III)



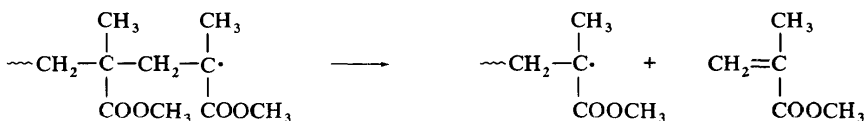
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With the examination of an increasing number of acrylate and methacrylate polymers and especially with the availability of modern analytical techniques which has made accurate analysis of minor products possible, it has become clear that the whole range of behaviours of acrylates and methacrylates can be described in terms of a single overall mechanism and that the differences observed depend simply upon the relative importance of the various constituent parts of the overall mechanism.

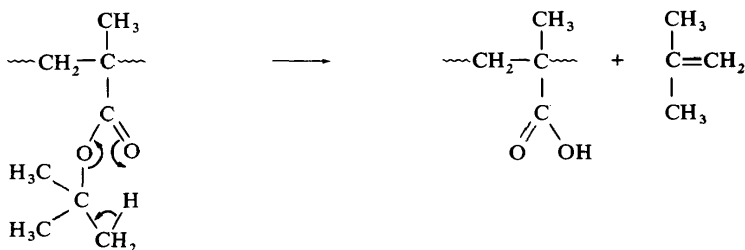
Photodegradation studies have also contributed to our new understanding of these reactions but since this aspect is to be discussed by my colleagues elsewhere in this conference, the present paper is confined to thermal degradations.

Methacrylate homopolymers

A great deal has been written about the thermal degradation of poly(methyl methacrylate)³. Radicals are formed either by scission of the molecules at random or at vulnerable chain terminal structures. These radicals then unzip to give very high yields of monomer.



With higher methacrylate esters, ester decomposition reactions become possible resulting in methacrylic acid units in the polymer and evolution of the corresponding olefin. The most thoroughly studied system of this kind is poly(*tert*-butyl methacrylate)² and it seems to be generally agreed that the reaction proceeds by a molecular mechanism involving interaction between the carbonyl group and hydrogen atoms on the β carbon atom of the ester group



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Although yields of isobutene from poly(*tert*-butyl methacrylate) are almost quantitative, the rate of evolution of volatile products during the course of the reaction turns out to be quite complex as shown in *Figure 1*. Analysis

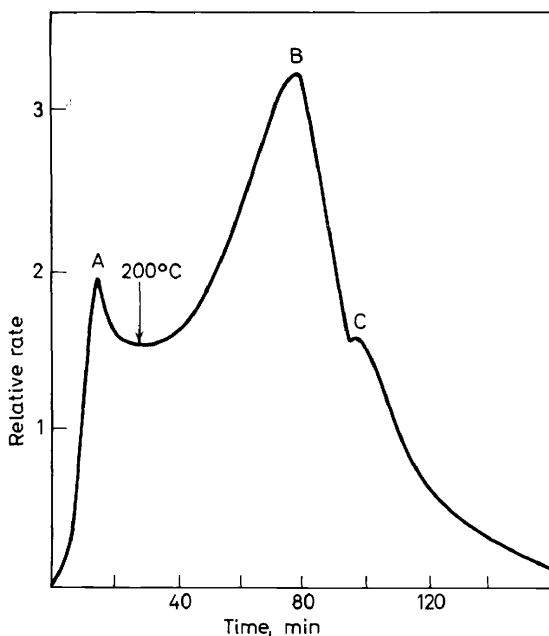


Figure 1. Rates of evolution of volatile products from poly(*tert*-butyl methacrylate) heated to and maintained at 200°C.

of these volatile products during the course of the reaction reveals that the main peak (B) is due to isobutene and the shoulder (C) to water eliminated in the conversion of the methacrylic acid residues to methacrylic anhydride. But the initial peak (A) is due to pure monomer amounting to about one per cent of the original polymer although no monomer is detectable among the products thereafter. The most obvious explanation is that unzipping to monomer occurs initially but that the reaction is soon very effectively blocked by the ever increasing concentrations of ester decomposition residues, acid or anhydride, in the polymer chains.

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	<i>n</i> -Propyl	2	iso-Propyl	6
iso-Butyl	1	<i>n</i> -Butyl	2	sec-Butyl	5
Ethoxyethyl	2	<i>n</i> -Hexyl	2	tert-Butyl	9
		<i>n</i> -Heptyl	2		
		<i>n</i> -Octyl	2		

The importance of β hydrogen atoms in facilitating ester decomposition at the expense of depolymerization is illustrated by the data in *Table 1*. Thus ester decomposition only becomes important when the monomer unit incorporates five β hydrogen atoms and depolymerization is quantitative when there are at most one or two β hydrogen atoms. Inhibition of ester decomposition in the ethoxy ethyl ester is probably assisted by the electronegativity of the oxygen atom adjacent to the β carbon atom which inhibits the movement of a β hydrogen atom as a proton towards the carbonyl oxygen as required by the ester decomposition mechanism.

Acrylate homopolymers

In a recent study of the thermal degradation of a series of poly(alkyl acrylates)⁴ thermal volatilization analysis (TVA) provided a useful preliminary picture of the reactions involved.

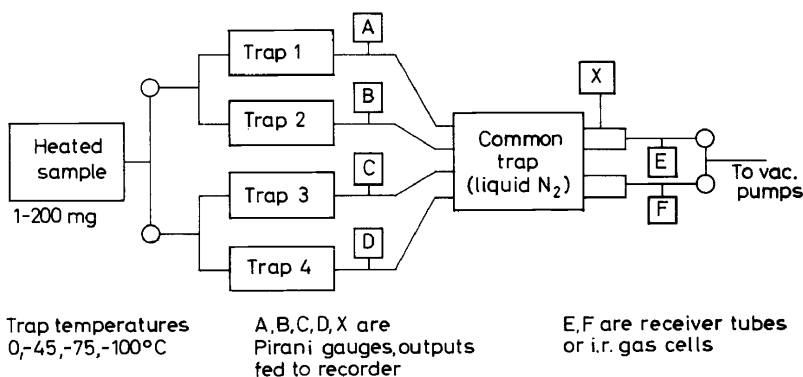


Figure 2. TVA with differential condensation.

The principle of TVA is illustrated in *Figure 2*. A sample of polymer is heated from 20° to 500°C *in vacuo* and the volatile products are passed through four traps in parallel. These traps are normally maintained at 0°, -45°, -75° and -100°C. Immediately after each trap a Pirani gauge measures continuously the pressure of volatile products passing through the trap. Thus the four gauges will record all products volatile at 0°, -45°, -75° and -100°C, respectively. The result is finally displayed by a pen recorder. TVA thermograms were obtained for polymers of methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl and 2-ethyl hexyl acrylates.

It is immediately clear that poly(iso-propyl) methacrylate, which is a secondary ester, behaves differently from the other polymers, which are all primary esters. As shown in *Figure 3*, volatilization is discernible in poly(iso-propyl acrylate) at 260° building up to a maximum of 355°C. A secondary peak occurs at 442°C. The behaviours of the five primary esters are very similar to one another and are typified by the *n*-butyl ester in *Figure 4*. They are more stable than the isopropyl ester, volatilization only becoming appreciable at 300°C and they exhibit only a single main peak. The coinci-

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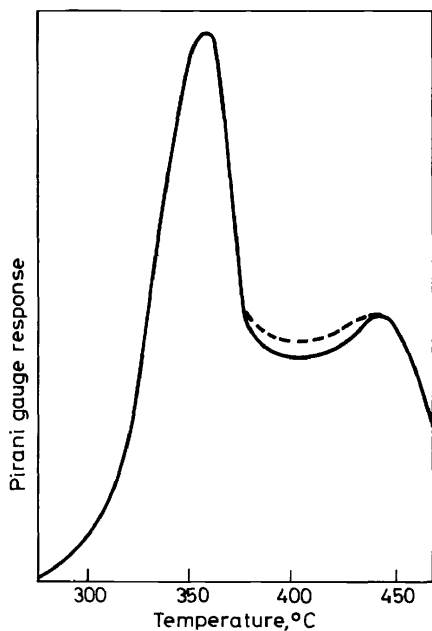


Figure 3. TVA thermogram of poly(iso-propyl acrylate): Trap temperatures, —, 0°C, - 45°C and - 100°C; ---, - 75°C.

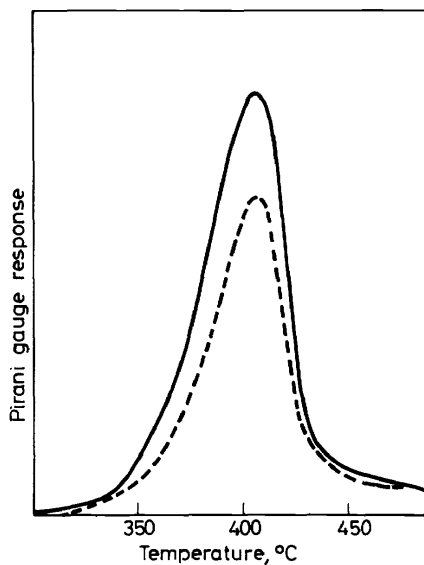
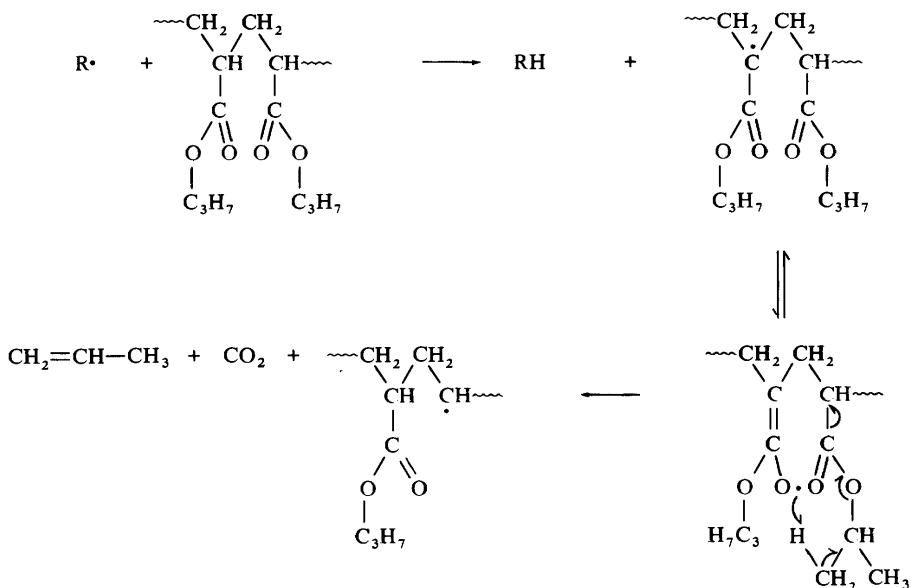
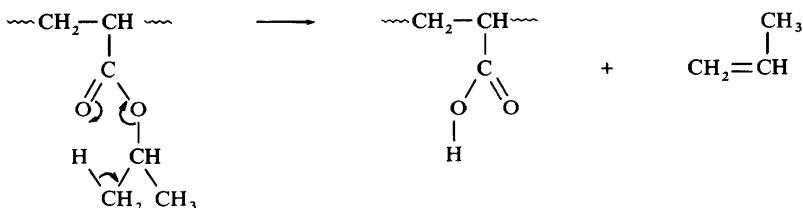


Figure 4. TVA thermogram of poly(*n*-butyl acrylate): Trap temperatures, —, 0°C and - 45°C; ---, - 75°C and - 100°C.

dence of all the traces in the thermogram of the iso-propyl ester indicates that all the products volatile at ordinary temperature are also volatile at -100°C . Quantitative analysis of the reaction products demonstrates that the only major products associated with the main TVA peak are carbon dioxide and propylene. Thus it is clear that the reaction associated with the main peak is ester decomposition combined with decarboxylation. This is quite different from the situation in poly(tert-butyl methacrylate) in which quantitative ester decomposition to form acid by a molecular mechanism is followed by quantitative elimination of water to form anhydride. It is suggested that at the higher temperature of the poly(iso-propyl methacrylate) decomposition reaction occurs principally by a radical mechanism as follows:



This mechanism predicts a carbon dioxide/propylene ratio of unity. However, the observed ratio is 0.6 so that a certain proportion of ester decomposition probably occurs by way of the molecular mechanism.



This is confirmed by the observation of anhydride structures in the residual polymer.

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A very much more complex mixture of products was obtained from the primary esters studied, namely the polymers of ethyl, *n*-propyl, *n*-butyl and 2-ethyl hexyl acrylates. There are fairly wide variations in the relative yields of the various products, but, as previously suggested by the TVA thermograms, the range of products from each polymer is qualitatively similar so

 Table 2. Products of thermal degradation of poly(*n*-butyl acrylate)

Main products	Products in low yield	Trace products
Carbon dioxide, but-1-ene, butanol, chain fragments	Butyl acrylate, butyl methacrylate	Methane, ethane, propane, butane, ethylene, propylene, <i>cis</i> -2-butene, hydrogen, carbon monoxide

 Table 3. Mass balance table for degradation of poly(*n*-butyl acrylate) at 315°C

Degradation time, h	1	2	4	8	20	24	32
Products (wt % of initial polymer)							
Residue	90.3	84.6	74.6	67.2	55.8	35.2	33.9
Insoluble	5.3	6.0	5.6	13.1	29.6	33.6	33.9
Soluble	85.0	78.6	69.0	54.1	26.2	1.6	0
Chain fragments	7.7	4.1	11.1	11.5	16.3	17.1	21.7
Total liquids	0.4	2.2	10.6	9.8	19.8	28.7	29.6
Alcohol	0.2	1.6	2.6	9.0	17.6	19.6	20.7
Monomer	0.00	0.04	0.08	0.10	0.16	0.20	0.20
Methacrylate	0.00	0.00	0.03	0.04	0.05	0.03	0.05
Remaining liquids	0.02	0.6	7.9	0.7	2.0	8.9	8.6
Condensable gases	1.8	4.0	5.1	9.4	14.8	15.4	15.5
Carbon dioxide	0.5	1.9	2.0	4.2	8.3	9.1	9.6
Butylene	1.3	2.1	3.1	5.2	6.5	6.3	5.9
Non-condensables	0.1	0.0	0.2	0.5	1.1	1.1	1.2
Total volatiles	10.0	10.3	27.0	31.2	52.0	62.3	68.0
Total products	100.3	94.9	101.6	98.4	107.8	97.5	101.9

it is convenient to discuss the mechanisms of their formation in terms of one of the polymers and poly(*n*-butyl acrylate) has been chosen for this purpose. Products are recorded in *Table 2*. Complete analyses were carried out at various times of reaction at 315°C and are recorded on a mass balance basis in *Table 3*.

The production of but-1-ene and carbon dioxide are illustrated in *Figure 5*. As in the methacrylate esters the yields of olefin vary with the number of β hydrogen atoms. Thus most is produced from the ethyl ester, least from the 2-ethyl hexyl ester and similar intermediate amounts from the *n*-propyl and *n*-butyl esters. The ratio of olefin to carbon dioxide is of the order of unity over an appreciable part of the reaction although the relative carbon dioxide yield increases in the later stages.

Chromatograms of minor hydrocarbon products are illustrated in *Figure 6* and are clearly produced by fragmentation of the butyl group. Butane is the

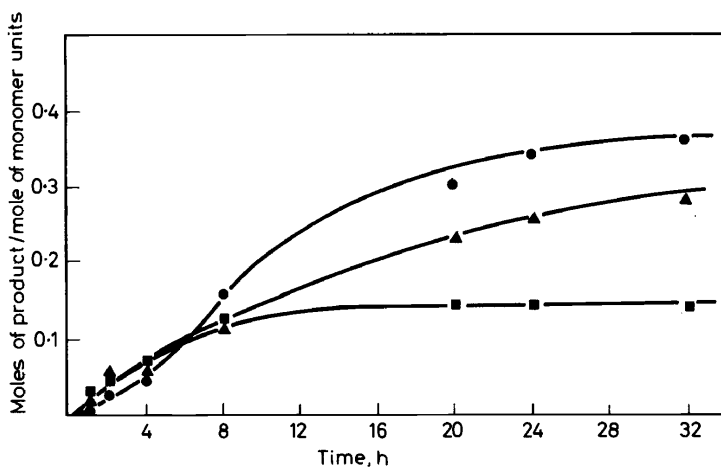


Figure 5. Production of carbon dioxide, ▲; 1-butene, ■; and *n*-butanol, ●, during degradation of poly(*n*-butyl acrylate).

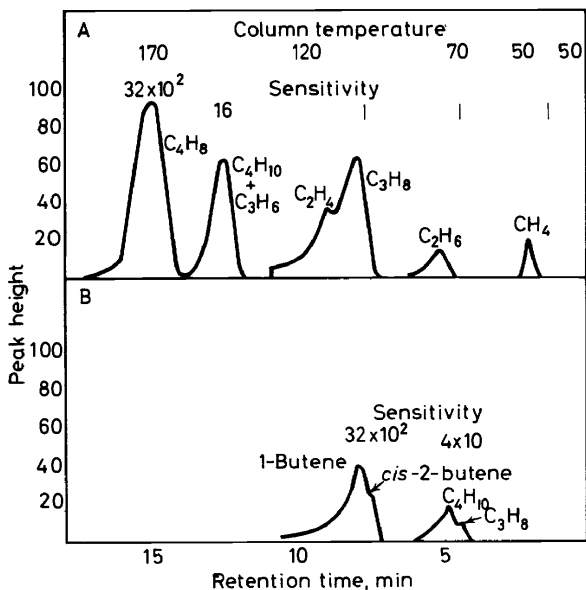


Figure 6. GLC of the gaseous products of degradation of poly(*n*-butyl acrylate): (A) on a silica gel column; (B) on a silver nitrate-benzyl cyanide column.

most abundant of these products but the olefin/alkane ratio always lies in the range 100/1 to 1000/1.

Butanol is the most abundant of the products liquid at ordinary temperatures. The monomer and the corresponding methacrylate monomer are produced in very much lower, although significant yield. The reaction curve

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for butanol is illustrated in *Figure 5* from which an autocatalytic tendency is discernible.

The chain fragment fraction is an oily material, volatile at degradation temperatures but involatile at ordinary temperatures. It is usually yellow,

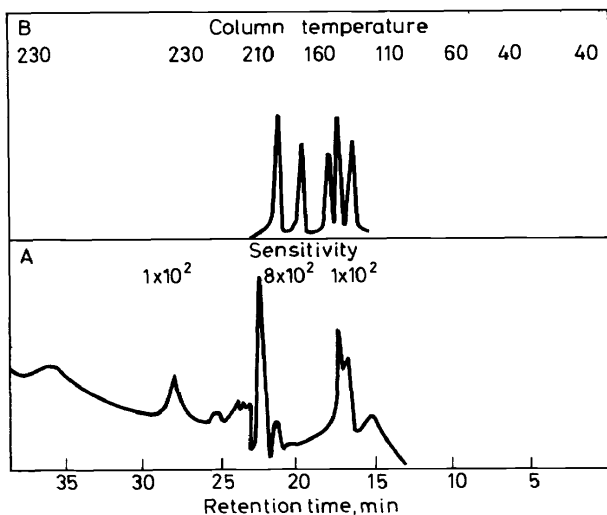


Figure 7: GLC, (A), of the chain fragments produced during degradation of poly(*n*-butyl acrylate) and (B), of a mixture of C_{18} , C_{19} , C_{20} , C_{22} and C_{24} *n*-alkanes for comparison.

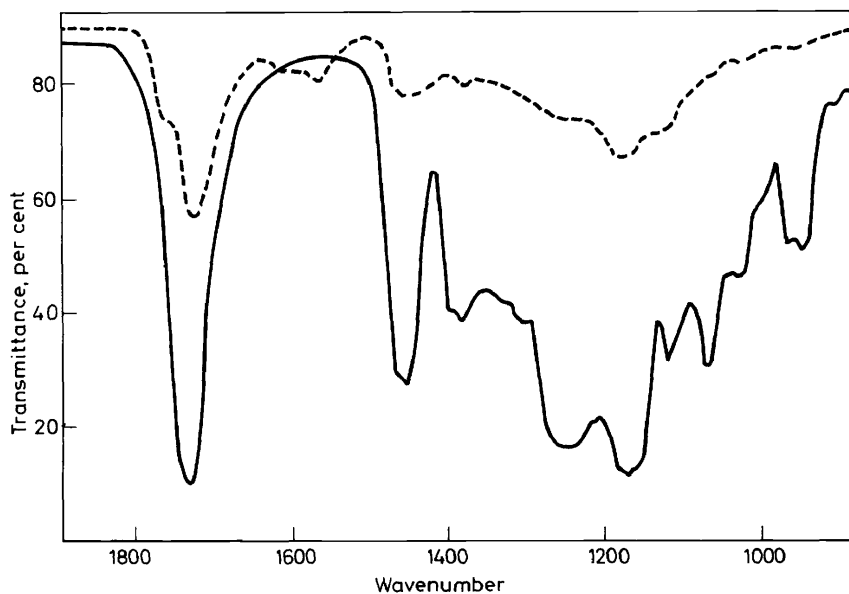


Figure 8. The $900\text{--}1900\text{ cm}^{-1}$ region of the infra-red spectra of undegraded, —, and degraded, ---, poly(*n*-butyl acrylate).

the intensity increasing with time of degradation. The infra-red spectrum is similar to that of the parent polymer although with some minor differences. The average molecular weight of the material obtained from the butyl ester was 470 which corresponds to three to four monomer units but it consists of a complex mixture as demonstrated by its chromatogram in *Figure 7(A)*. The order of the molecular weight is confirmed by the chromatogram of a mixture of C_{18} – C_{24} *n*-alkanes presented in *Figure 7(B)*.

Insolubility develops progressively in the residual polymer although there is a rapid decrease in the molecular weight of the soluble part. The insoluble part is insoluble in all common organic solvents and even on prolonged treatment with sodium hydroxide solution. Since the principal volatile products, carbon dioxide, olefin and alcohol, must be products of decomposition of the ester group one would expect to observe quite significant changes in the infra-red spectrum of the residue during degradation. The

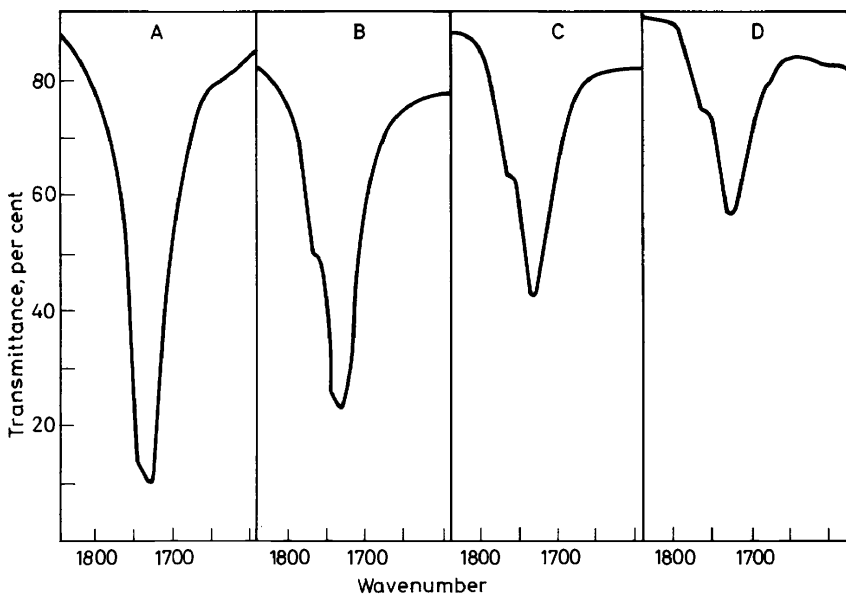


Figure 9. The carbonyl region of the infra-red spectrum of poly(*n*-butyl acrylate) during progressive degradation. A, undegraded; B, 4 hours; C, 8 hours; D, 16 hours.

900–1900 cm^{-1} region of undegraded and degraded poly(*n*-butyl acrylate) are compared in *Figure 8*. The principal changes are the development of a shoulder on the carbonyl peak at 1760 cm^{-1} , a general increase in absorption between 1650 and 1550 cm^{-1} and appearance of a new peak at 1563 cm^{-1} . There is a shift in the carbonyl maximum from 1730 to 1720 cm^{-1} and in the C—O stretch region from 1165 to 1175 cm^{-1} . Outside the 900–1900 cm^{-1} region there are no significant changes. Changes in the carbonyl region are illustrated in more detail in *Figure 9*.

The fraction described as 'remaining liquids' is probably mainly water.

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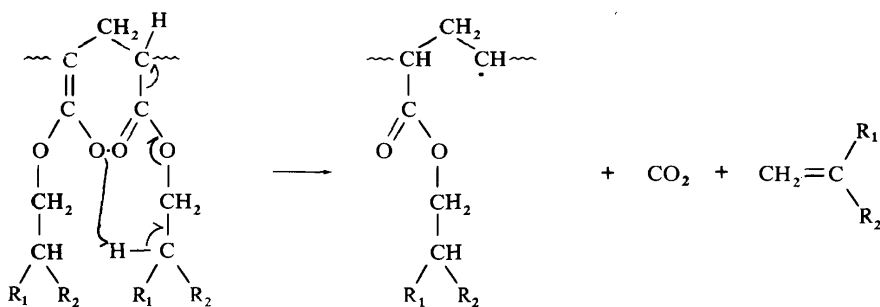
TVA and the data in *Table 3* have demonstrated that the principal characteristics of the production of all the degradation products are similar. Alcohol production, which exhibits slight autocatalytic properties, is a possible exception. It therefore seems probable that all the products must be accounted for in terms of a complex series of radical processes with a common initiation step. It has been suggested^{4, 5} that the initial step is exactly the same as that suggested for the poly(iso-propyl acrylate) degradation, resulting in the



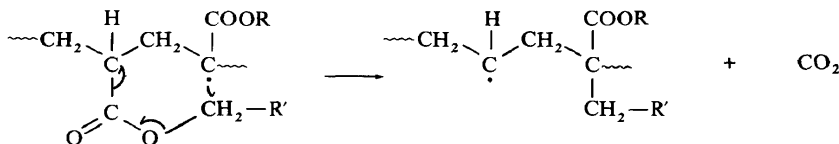
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relatively stable radical, A, and that all the major decomposition products are initiated by this radical.

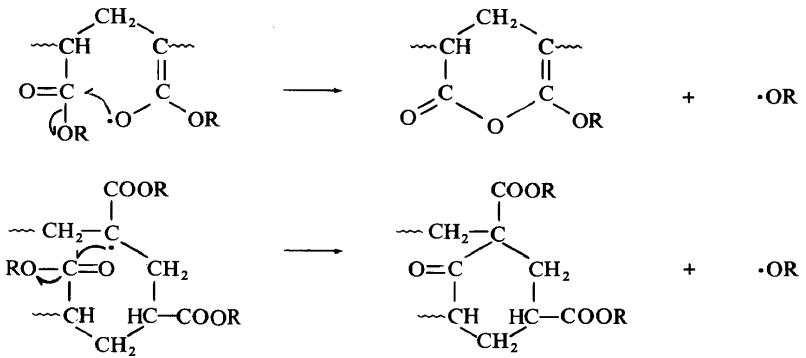
Carbon dioxide and olefin are produced from these polymers in a molar ratio close to unity, at least in the early stages of reaction. It therefore seems



probable that they are produced in a reaction exactly analogous to that proposed to account for the poly(iso-propyl acrylate) reaction. Unlike the poly(iso-propyl acrylate) reaction, however, carbon dioxide production exceeds that of olefin at longer reaction times. It has been suggested⁵⁻⁸ that this can be accounted for in terms of the following reaction:



Two possible mechanisms for the production of alcohol are represented in the following equations. In each case they are represented to occur intramolecularly although an intermolecular version is also possible. The first results in a γ, δ unsaturated δ lactone ring system while the second



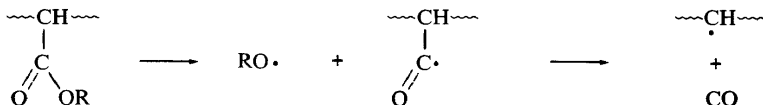
produces a β -ketoester. The former receives strong support from infra-red data. As shown in *Figure 9* a shoulder develops at 1760 cm^{-1} which is at higher frequency than most carbonyl absorptions and suggests the presence of a lactone. Normal absorption for δ lactones is in the region $1750\text{--}1735\text{ cm}^{-1}$ but with γ , δ unsaturation in the ring absorption could easily be moved to 1760 cm^{-1} .

Carbon-carbon double bond absorption is normally much weaker than carbonyl absorption. However, in this case the polarity of the bond will be greater because of the presence of two carbon-oxygen bonds at one end and two carbon-carbon bonds at the other end. This may explain the enhanced absorption in the carbon-carbon double bond region between 1680 cm^{-1} and 1620 cm^{-1} as degradation proceeds although no clear peak can be distinguished. However, the carbonyl absorption overlaps into this zone at later stages of degradation so no firm conclusions about the structure can be drawn from absorption in this region. The second route suggested for alcohol formation yields a saturated ketone which would absorb in the region $1720\text{--}1700\text{ cm}^{-1}$. This is slightly lower than the absorption of ester carbonyl so that the presence of ketonic structures in the degradation residue may explain the shift in the carbonyl peak to lower frequency.

Thus there is strong infra-red spectral evidence for lactone formation while changes in infra-red spectra are in accordance with, but do not prove, the formation of ketonic groups.

One striking feature of the production of alcohol is its apparent autocatalytic characteristics. The mechanisms proposed for alcohol production are all initiated by the same polymer radical as are the other component parts of the overall reaction and since no other part of the reaction is autocatalytic, there is no obvious direct chemical route by which the products of the alcohol elimination reaction might facilitate further production of alcohol. Alternatively, the answer may be associated with the changes in the physical nature of the polymer molecule brought about by elimination of alcohol. Both reactions proposed above involve either the formation of a ring (when they occur intramolecularly) or of a crosslink (when they occur intermolecularly). These new structures would decrease the flexibility of the polymer molecules and this should be expected to encourage intramolecular reactions involving six-membered rings such as those proposed for alcohol

Carbon monoxide is another minor product from all the polyacrylates studied. It must obviously be derived from the ester group and the most likely source is through homolytic scission of the acyl-oxygen bond,



The carbonyl radical is very unstable¹¹ and will decompose immediately to give carbon monoxide.

In view of the overlap in the behaviour of the polyacrylates and polymethacrylates it has been of interest to examine the reactions which occur in their copolymers and in particular in a series of methyl methacrylate-methyl acrylate and methyl methacrylate-*n*-butyl acrylate copolymers where a wide range of mole ratios have been examined^{8, 12}.

The products of decomposition of these copolymers are qualitatively what one would expect from the behaviours of the homopolymers but there are some quite significant features which throw further light on the nature of certain of the component reactions. Data for the methyl methacrylate-methyl acrylate system are presented in *Table 4*.

Table 4. Composition of volatile products of degradation of MMA-MA copolymers

Polymer	Composition, % by weight of total volatiles					
	CO ₂	Permanent gases	Methanol	MMA	MA	Chain fragments
PMMA	—	—	—	96	—	—
112/1	Trace	—	—	96	—	Trace
26/1	1	Trace	—	93	0.8	5
7.7/1	1	0.1	—	87	2.5	10
2/1	3	0.4	—	64	7.0	25
PMA ^a	7.5	1	15	—	0.76	75

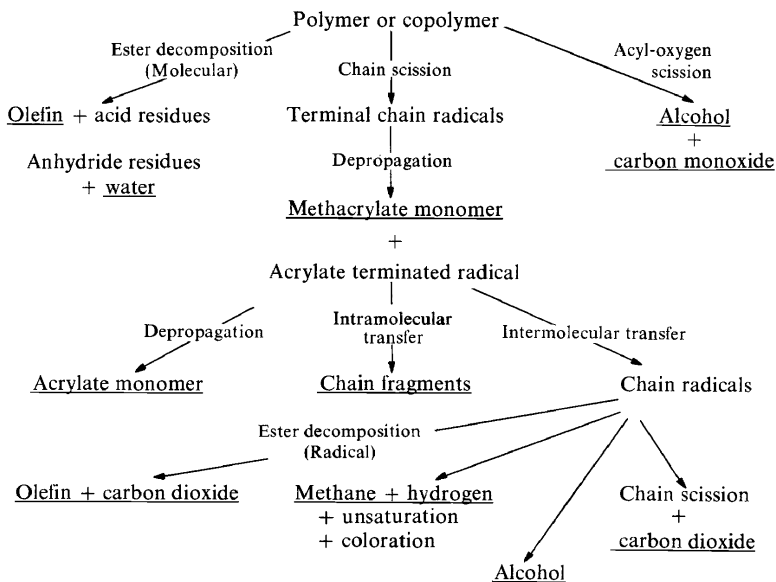
The high yields of alcohol, typical of the primary acrylates, are drastically reduced by incorporation of methyl methacrylate. The effect of methyl methacrylate units is to break up the methyl acrylate units into short sequences and calculations demonstrate that at least three acrylate units are required in sequence in order that alcohol be formed. This conclusion is in accordance with the thermal degradation behaviour of ethylene-methyl acrylate copolymers¹³. Thus block copolymers produce methanol in the quantities expected from the methyl acrylate content while random copolymers of the same overall composition produce very much less.

It may also be surprising that the yield of methyl acrylate increases with decreasing concentrations of acrylate in the copolymer. It seems that single acrylate units can readily participate in an unzipping process but that unzipping cannot pass through groups of methyl acrylate units. In this

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case transfer reactions are preferred which is reflected in the strong tendency for the yield of chain fragments to increase with acrylate content.

Thus studies to date allow the following integrated mechanism for the thermal degradation of polyacrylates, polymethacrylates and acrylate-methacrylate copolymers to be drawn up (volatile products are underlined).



The pattern of products obtained from any given polymer or copolymer will depend upon the interplay of all these processes which, in turn, is determined by structural factors as outlined in this paper. Further studies may, of course, necessitate additions or modifications to the reaction scheme.

One may summarize the application of this reaction scheme to the thermal degradation of polyacrylates, polymethacrylates and acrylate-methacrylate copolymers in the following way.

1. If the number of β hydrogen atoms is large as in the tert-butyl esters then ester decomposition by the molecular mechanism occurs preferentially giving the corresponding olefin and acrylic or methacrylic acid units in the polymer.
2. When fewer β hydrogen atoms are present, a higher temperature is required for the molecular mechanism and radical processes occur preferentially.
3. Among the methacrylates chain scission to form radicals is followed by unzipping to monomer although the yields of monomer may be limited by small amounts of ester decomposition, the extent of which depends upon the β hydrogen atom content.
4. Among the polyacrylates radical induced ester decomposition predominates if the monomer has a large number of β hydrogen atoms as in poly(iso-propyl acrylate).

5. In polyacrylates with fewer β hydrogen atoms a much more complex series of reactions occurs in competition with ester decomposition yielding the alcohol corresponding to the ester group and chain fragments as major products and the monomer, the corresponding methacrylate, hydrogen and carbon monoxide as the principal minor products.
6. Products of degradation of acrylate-methacrylate copolymers are usually qualitatively what one would expect from the behaviours of the individual homopolymers although alcohol, monomer and chain fragment yields are strongly dependent upon copolymer composition.

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