I

QUANTITATIVE ASPECTS OF PYROLYSIS/GAS–LIQUID CHROMATOGRAPHY OF SOME VINYL POLYMERS

H. McCORMICK

I.C.I. Ltd., Paints Division, Wexham Road, Slough, Bucks. (Great Britain)

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SUMMARY

Using a filament type pyrolyser and a specially constructed control unit, the depolymerisation behaviour of acrylates, methacrylates and styrene homopolymers and copolymers was examined by "stepwise" and "one shot" pyrolysis under controlled conditions.

The possibility of pyrolysis/gas–liquid chromatography as a technique for distinguishing mixtures of homopolymers from copolymers as well as for quantitative measurements is shown.

Some theoretical considerations of thermal degradation of vinyl polymers are also given.

INTRODUCTION

From the mass of information on thermal degradation of vinyl polymers[1,4–8,10–15] it may be concluded that such polymers have an optimum depolymerisation temperature at which a maximum monomer yield is obtained. Above this temperature the monomer yield decreases, with the formation of secondary and higher breakdown products. An example of this is in the work of MADORSKY AND STRAUS[1], who examined the breakdown products of polystyrene between 360° and 850° by mass spectrometry and found that at 360° 94.4 % of the volatile products consisted of monomer and 5.6 % toluene, whereas at 850° the volatile products contained 34 % monomer, 58.2 % benzene, 5.5 % toluene and 1.9 % propadiene. Generally this behaviour was confirmed by LEHMANN AND BRAUER[2], who examined the depolymerisation products by pyrolysis/gas–liquid chromatography.

It appears, therefore, to be a justifiable assumption that if a high monomer yield and avoidance of the formation of secondary and higher breakdown products is sought it would be advisable to carry out depolymerisation within a certain temperature range.

The primary aim of this work was to establish such depolymerisation conditions and investigate the quantitative aspects of the behaviour of acrylic polymers and copolymers on depolymerisation. In the course of this work, however, it was found that such polymers have characteristic depolymerisation patterns which make it

possible to distinguish between mixtures of homopolymers and copolymers. Further work on polymers of known composition would undoubtedly be necessary in order to elucidate certain breakdown behaviour, but the aim of this paper is to illustrate the practical usefulness of the technique used.

EXPERIMENTAL

Apparatus

The pyrolyser. This is a coil made from 9 cm of 30 S.W.G. nichrome wire wound on a No. 6 wood screw and spot welded to tungsten leads into a B7 cone (Fig. 1a). The hollow part of the cone is filled with an aqueous solution of sodium silicate and allowed to solidify. The cone is placed into the inlet of a Perkin-Elmer F11 gas chromatograph provided with a B7 socket (Fig. 1b).
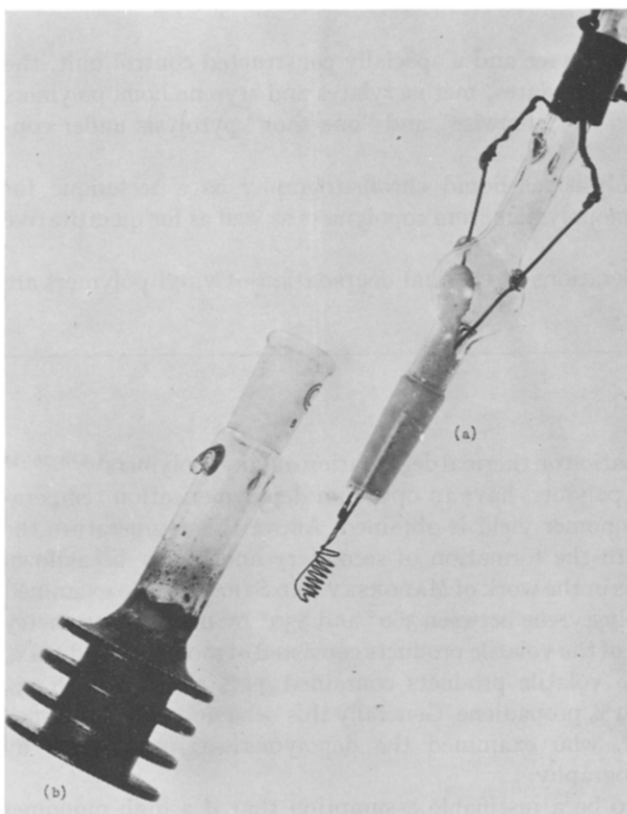

Fig. 1. The pyrolyser used in this work.

The pyrolyser control unit. This unit is basically that described by BARLOW, LEHRLE AND ROBB[3] in which the selector switch giving coil temperature increments of 100° between 150° and 950° was replaced by a variable resistance (Variac) allowing pyrolysis to be made at any desired temperature. The unit also controls a booster which brings the initial temperature of the coil to just below the breakdown tempera-

ture of the polymer and may also be used to evaporate any residual solvent prior to depolymerisation. Provisions for the control of the length of time of the electrical impulse ("flashing time") and burning off the polymer residues at a high temperature are also incorporated.

Once the desired conditions are set, the depolymerisation sequence is performed automatically by pressing the push-button marked "prime" on the top left side of the depolymerisation unit (Fig. 2).

The gas chromatograph used was a Perkin-Elmer F11 with temperature programming and a flame ionisation detector. The inner tube carrying the gas to the column was extended so as to be approximately 2 mm from the end of the coil.

A 2 m column, packed with 20 % polyester (DEGS) on Celite (60–80 mesh) was used throughout this work except in the case of methyl methacrylate/ethyl acrylate copolymers when a 4 m 20 % silicone oil column was used.
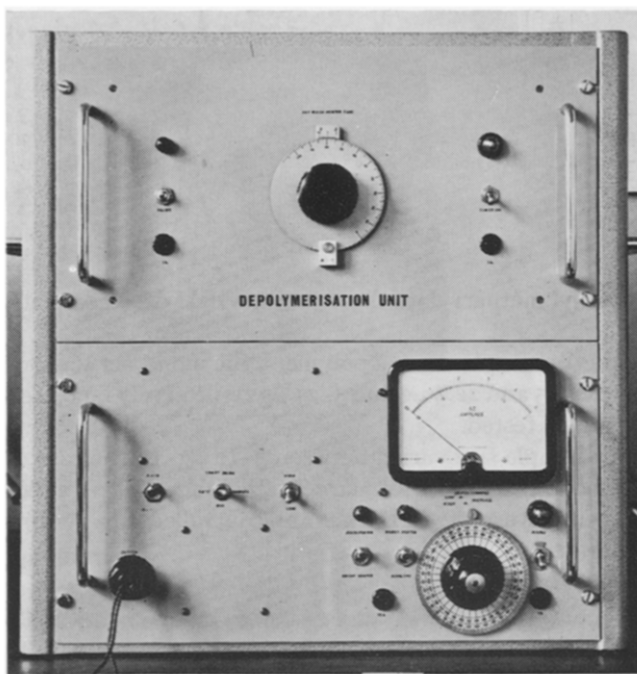

Fig. 2. The pyrolyser control unit.

Depolymerisation conditions

Depolymerisation temperature. The average temperature of the coil at any setting of the "Variac" was found by calibrating with compounds of known melting points. The temperature, however, varies along the length of the helix and in order to obtain reproducibility, the sample, in solution, was always placed on the smallest turn of the helix. Although this ensured reproducibility, the temperature should not be regarded as the true temperature.

Flashing time. The influence of the length of time of the electrical impulse (flashing time) was investigated using methyl methacrylate, styrene and ethyl

acrylate homopolymers. In each case when the same weights of the samples (10 μg) were depolymerised under individually identical conditions but with flashing times of 10, 20 or 30 sec, no differences were observed in the shapes or heights of the peaks of the individual monomers evolved. It was, therefore, concluded that, for this weight, the depolymerisation took place within the first 10 sec of flashing and this time was used in all subsequent work.

Sample weight. It is reasonable to assume that the smaller the sample the more efficient the depolymerisation.

The effect of the sample weight on the monomer yield of polymethyl methacrylate is shown in Table I. Samples of 1, 2, 3, 4 and 5 μl of a solution containing 2.52 μg/μl of polymethyl methacrylate in benzene were depolymerised at the optimum temperature in duplicate.

TABLE I

Weight (μg) depolymerised	% of monomer yielded
2.52	100* ± 1.0
5.04	95.0 ± 1.1
7.56	88.5 ± 0.0
10.08	83.5 ± 2.5
12.60	73.0 ± 1.1

* Assumed 100 %.

Thus in the case of polymethyl methacrylate the monomer yield decreases with increasing sample size.

In the case of styrene and ethyl acrylate homopolymers, the monomer yield of samples varying in weight between 4.5 and 22.5 μg and 5–25 μg respectively increased steadily with weight within the ranges tested.

Generally in this work, the sample size varied between 5–10 μg. In the case of acrylates, however, because the monomer yield is low, larger sample size was required.

Carrier gas flow rate. Nitrogen was used as carrier gas and controlled by a Perkin-Elmer flow control unit at 25 ml/min.

Depolymerisation procedure

In order to find the optimum depolymerisation temperature samples were depolymerised in steps at increasing temperatures and the monomers evolved recorded. Two procedures were followed:

(i) In the first a known volume of polymer solution of known concentration was placed in the smallest turn of the helix using a 10 μl Hamilton syringe. The helix was placed in the B7 socket of the chromatograph and the booster switched on in order to flash off the solvent. When the chromatograph reached stable conditions, the sample was depolymerised at 250° and the monomer evolved recorded. The coil was then removed and cleaned by burning off the residue. It was then recharged and the same procedure repeated at 25° increments.

(ii) Because this procedure was too lengthy, a second procedure of stepwise depolymerisation was tried. In this procedure the residue from the pyrolysis at a lower temperature was used for the next step until complete depolymerisation was

achieved. The stepwise depolymerisation of polymethyl methacrylate by the two techniques is illustrated in Fig. 3. The traces show the peak areas of the monomers evolved plotted against temperature. Fig. 3a, which is the first type of depolymerisation, shows a maximum monomer evolution at 410° after which the monomer yield decreases with temperature, while the stepwise depolymerisation, Fig. 3b, appears similar to the first derivative of the first procedure. This second procedure was used in all subsequent work.
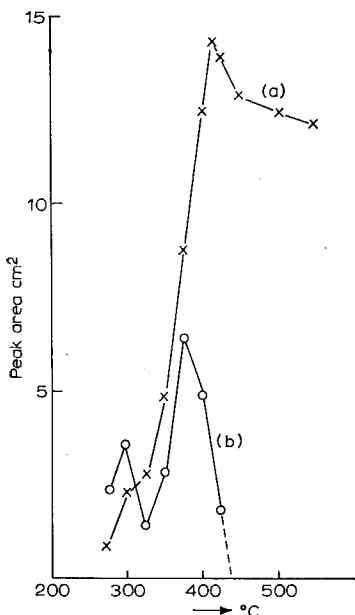

Fig. 3. (a) Constant weight and (b) stepwise depolymerisation of polymethyl methacrylate.

RESULTS

Distinction between copolymers and homopolymer mixtures

Applying the stepwise depolymerisation procedure to various polymers it was found possible, because of the differences in the depolymerisation temperature, to distinguish copolymers from mixtures of homopolymers (Figs. 4–6).

The stepwise depolymerisation procedure is thus a useful method for distinguishing mixtures of homopolymers from copolymers. Once this is established, the unknown polymer may, thereafter, be depolymerised at one temperature (its optimum temperature) by 'one shot' depolymerisation. The two procedures, however, do not give identical yields. Some results obtained by the two techniques are given in Table II and will be discussed later in considering the mechanism of depolymerisation.

Monomer yield of copolymers on one shot depolymerisation

The monomer yield obtained from homopolymers is not repeated in their copolymers. Indeed the trend in Table II is reversed and higher yields of acrylates
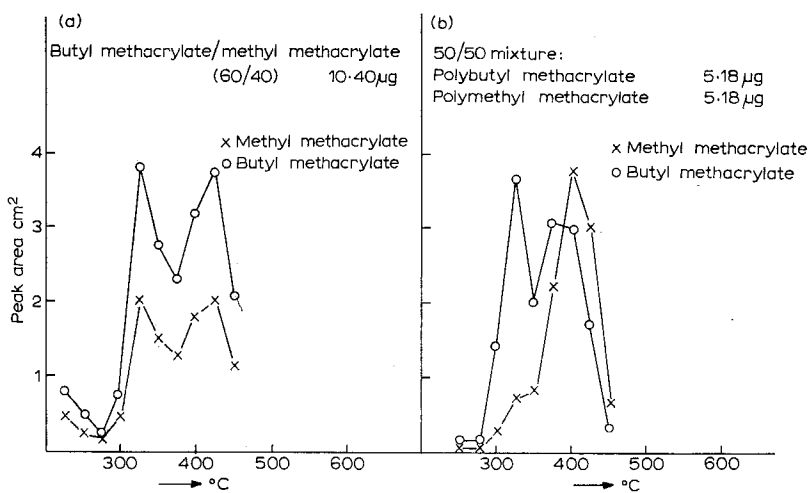
Fig. 4. Stepwise depolymerisation of (a) polybutyl methacrylate/methyl methacrylate copolymer and (b) a mixture of homopolymers.
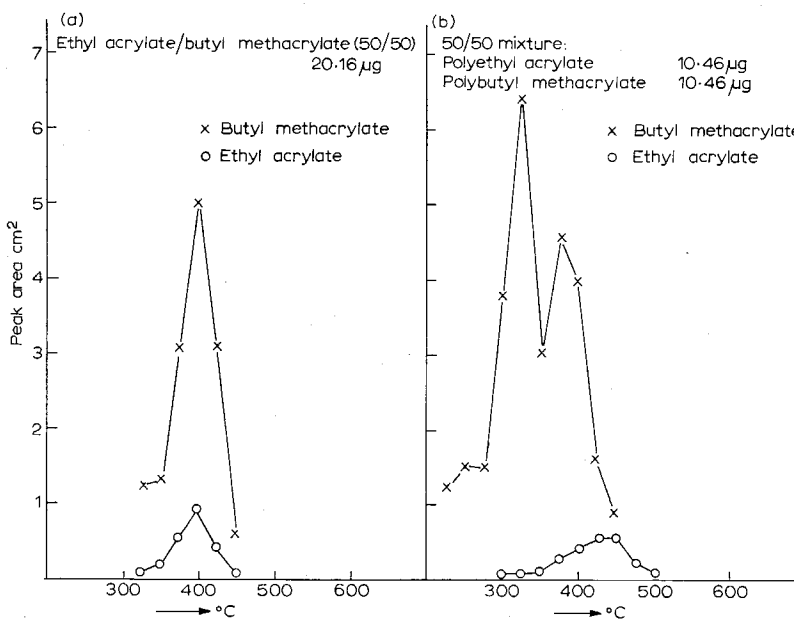

Fig. 5. Stepwise depolymerisation of (a) polyethyl acrylate/butyl methacrylate copolymer and (b) a mixture of homopolymers.
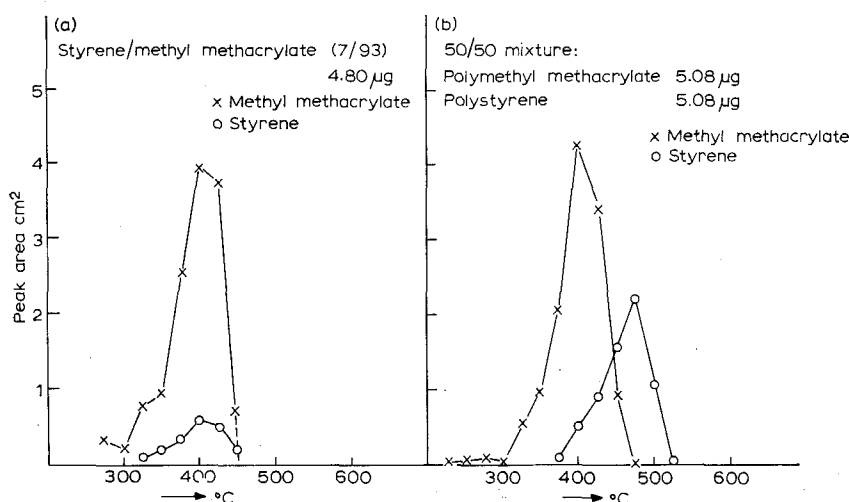
Fig. 6. Stepwise depolymerisation of (a) polystyrene/methyl methacrylate copolymer and (b) a mixture of homopolymers.

TABLE II

Polymer	% monomer yield	
	One shot	Stepwise[b]
Polymethyl methacrylate, mol.wt. 35,000	49.5	63.3
Polymethyl methacrylate, mol. wt. 216,000	50.0	74.7
Polybutyl methacrylate[a]	95.0	95.0
Polyethyl acrylate[a]	7.0	6.6
Poly-2-ethylhexyl acrylate[a]	12.0	2.5
Polystyrene[a]	48.6	49.0

[a] Molecular weight unknown.
[b] Summed total.

and lower yields of styrene and methacrylates are obtained from copolymers as shown in Table III.

Since the monomer yield varies so greatly with the type of polymer, one would assume at first glance that quantitative estimation would be impossible. However, a linear relationship can be shown to exist between the ratio of the monomers in the polymer and the ratio of the peak areas of the monomers evolved as is shown in Table IV and illustrated in Figs. 7, 8 and 9.

Thus quantitative analysis is possible provided it is first ascertained that the material is a copolymer and not a mixture of homopolymers. The extension of this conclusion to other copolymers, multi-component polymers and block copolymers has not been checked, but it seems reasonable to assume that block copolymers would behave like a mixture of homopolymers. In preparing calibration graphs of multi-component polymers, in order to provide valid quantitative estimation, only one of the components should be varied at a time.

TABLE III

ONE-SHOT DEPOLYMERISATION OF A SERIES OF HOMOPOLYMERS AND COPOLYMERS AT 500°

Polymers	% monomer yield (on polymer)	
	Ethyl acrylate	*Methyl methacrylate*
Methyl methacrylate homopolymer	—	50.0
Ethyl acrylate homopolymer	7.0	—
Ethyl acrylate/methyl methacrylate (80/20)	15.4	18.5
Ethyl acrylate/methyl methacrylate (70/30)	17.2	20.6
Ethyl acrylate/methyl methacrylate (25/75)	67.0	38.6
	Ethyl acrylate	*Butyl methacrylate*
Butyl methacrylate homopolymer	—	95.5
Ethyl acrylate/butyl methacrylate (50/50)	36.8	59.3
	Ethyl acrylate	*Styrene*
Styrene homopolymer	—	48.6
Ethyl acrylate/styrene (77/23)	19.1	41.6
Ethyl acrylate/styrene (7/93)	25.0	57.0
	2-Ethylhexyl acrylate	*Methyl methacrylate*
2-Ethylhexyl acrylate homopolymer	12.0	—
2-Ethylhexyl acrylate/methyl methacrylate (60/40)	19.0	39.0
2-Ethylhexyl acrylate/methyl methacrylate (40/60)	33.6	50.0
	Butyl acrylate	*Methyl methacrylate*
Butyl acrylate/methyl methacrylate (80/20)	11.4	21.8
Butyl acrylate/methyl methacrylate (20/80)	36.4	42.6
	Styrene	*Methyl methacrylate*
Styrene/methyl methacrylate (7/93)	96.0	63.0
	Butyl methacrylate	*Methyl methacrylate*
Butyl methacrylate/methyl methacrylate (60/40)	97.0	50.6

TABLE IV

Ratio of monomers in the polymer (A)		Ratio of peak areas of respective monomers evolved (B)	Ratio A/B
Ethyl acrylate/styrene			
(77/23)	3.35	0.43	7.8
(7/93)	0.075	0.01	7.5
Ethyl acrylate/methyl methacrylate			
(80/20)	4.0	0.92	4.35
(70/30	2.33	0.54	4.31
(25/75)	0.33	0.16	2.06[a]
Methyl methacrylate/butyl acrylate			
(85/15)	5.67	10.0	0.57
(75/25)	3.00	5.2	0.58
(65/35)	1.86	3.2	0.58

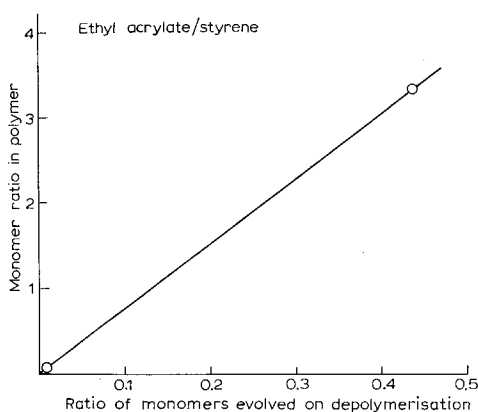[a] In this case it is suspected that not all the ethyl acrylate was in polymeric form.
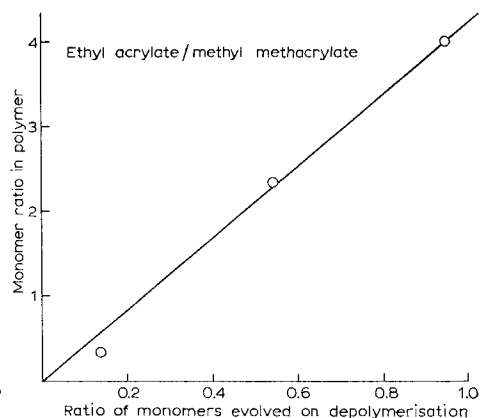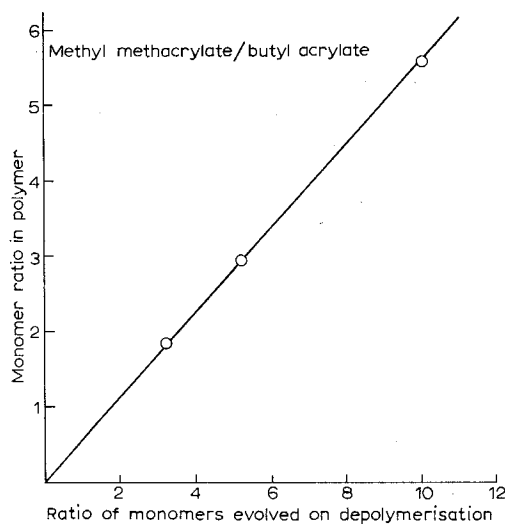
Fig. 7.

Fig. 8.

Fig. 9.

DISCUSSION

Mechanism of depolymerisation

On trying to explain the mechanism of depolymerisation some understanding of the thermal degradation process is necessary.

There are a number of possibilities that could govern the thermal degradation of polymers:

(I) The bonds in the chain may be broken at random, each bond being of equal strength and accessibility[4].

(2) There may be a number of weak links in the chain which are more easily ruptured than the normal bonds[5].

(3) The weak links may induce reactions which activate the weak points and split off a number of monomer units[6].

(4) The degradation may be caused by an activation of the chain ends followed by a rapid splitting off of the monomer units (propagation reaction)[7].

The thermal stability of a polymer and the breakdown products obtained on pyrolysis may be related in part to the relative strengths of the $-C-C-$ bonds, thus:

$$C-C-C \; > \; \underset{\displaystyle \underset{C}{|}}{C-C-C} \; > \; \underset{\displaystyle \underset{C}{|}}{\overset{\displaystyle \overset{C}{|}}{C-C-C}}$$
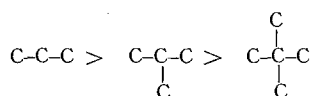
In the case of polyethylene chains, experimental results show that the more hydrogen atoms in the chain are substituted and the larger these side groups, the greater the monomer yield on depolymerisation. According to MADORSKY[9] polyethylene has a monomer yield of 0.03 %, polypropylene 0.17 %, polyisobutylene 18.1 %, polystyrene 40.6 % and polymethylstyrene 100 %.

GRASSIE AND MELVILLE[10] investigating the thermal degradation of methyl methacrylate polymers of various molecular weights found that for a polymer of molecular weight of 44,300 (I) the molecular weight of the residue remained constant up to 65 % degradation.

In the case of polymers of molecular weight 94,000 (II) and 179,000 (III), the molecular weights of the residues remained constant up to 30 % and 20 % degradation respectively after which they dropped sharply to approximately 70–80 % of the original value at about 60 % degradation.

In the case of a polymer of molecular weight 725,000 the molecular weight of the residue dropped linearly to 40 % of the original value at 60 % degradation. HART[11] similarly found that a polymer of molecular weight 5,100,000 at 10 % degradation gave a residue with a molecular weight of one-third of its original value.

This would indicate that the higher the molecular weight of the polymer the greater the drop in the molecular weight of the residue on partial depolymerisation. According to GRASSIE AND MELVILLE[10] this degradation behaviour of high molecular weight polymers indicates a random scission followed by an unzipping process where monomers split off the chain ends one at a time. In the case of polymers, (I), (II) and (III) above, the assumption is that a steady state is reached in the first stage of depolymerisation because of the rapid disappearance of the short chain polymer. It would thus appear that there are two mechnisms at work and this might explain the double peaks obtained in some stepwise traces (Figs. 3–5).

The degradation of polymethyl methacrylate is thus believed to be mainly governed by random scission. These scissions are not accompanied by a hydrogen transfer because of the steric hindrance of $-CH_3$ and $-COOCH_3$ on every alternate carbon which is quaternary. The scission thus results in the formation of free radicals which once initiated unzip completely. In this way only monomers appear in the pyrolyzate.
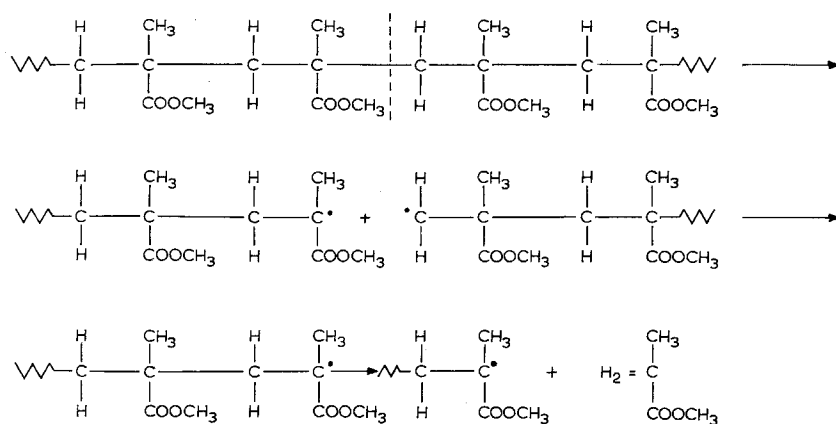
In the case of polystyrene, STAUDINGER AND STEINHOFER[12] examined the degradation and found that in addition to monomer, dimers and higher units were also formed and postulated a mechanism of scission at weak links to explain the formation of such units.

Since the bonds between hydrogen and tertiary carbon are weaker than those between hydrogen and secondary carbon the formation of fragments larger than monomer takes place:
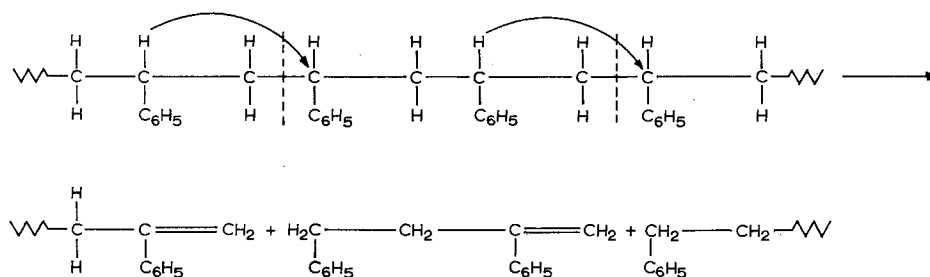
Similarly higher units may be formed. However, not all scissions result in unsaturated ends. In some cases the break results in free radicals which will unzip to yield monomers. Thus, styrene polymers, in addition to chain scission at weak links, also depolymerise by an unzipping process and consequently monomers, dimers and higher units are formed.

Support of the theory of weak links in the case of polystyrene is given by GRASSIE AND FARISH[15]. They examined the molecular weight of the residue on degrading a polymer of molecular weight 73,000 and found that after 20 % degradation the molecular weight dropped to just below 20 % of the original, the molecular weight falling very sharply in the initial stages of depolymerisation.

It is interesting to note that polystyrene both on stepwise and one shot pyrolysis gave similar results (49 % monomer yield, see Table II). This figure is in reasonable agreement with the theoretical value of 56 %[15].

In the case of acrylate polymers the degradation mechanism does not favour the

formation of free radicals as in methacrylates. STRAUS AND MADORSKY[13,14] studied the thermal degradation of polymethyl acrylate by mass spectrometry and found the monomer yield to be 0.7 % of the total volatiles among which were considerable amounts of carbon dioxide, methanol and long-chain fragments. Our results by pyrolysis/GLC of acrylates show the respective alcohol to predominate over the monomer but the yield of the latter depends on the depolymerisation conditions. The yield obtained by one shot was higher (6–12 %) than that obtained by stepwise depolymerisation (2.5–6 %).

From what is known of the degradation of homopolymers, it is anticipated that the degradation behaviour of copolymers would be dominated by that of the major constituent. The extent of these influences in the case of thermal degradation of styrene/ methyl methacrylate copolymers has been studied by GRASSIE AND FARISH[15]. It was found that the number of weak links in the copolymer was proportional to the amount of styrene and that a sequence of at least ten styrene units was necessary in the copolymer molecules to produce dimers, trimers and tetramers. As a consequence a higher monomer yield of styrene was anticipated from copolymers with low styrene content.

Using the reactivity ratios based on the copolymerisation theory[16,17] they calculated the sequence of styrene units present in the copolymers used.

It was thus worked out that for a 1/4 styrene/methyl methacrylate copolymer 87 % of the polymer contained single units and 11.7 % double units. For a 10/1 styrene/methyl methacrylate copolymer only 1.0 % were single units and 71.9 % were above ten units.

If it is assumed that all styrene sequences up to ten units yield only monomers and above ten give the characteristic breakdown of pure polystyrene, the monomer yield for 10/1 styrene/methyl methacrylate would be 60 % and for 1/4 styrene/methyl methacrylate nearly 100 %. In this work the yield obtained for a 7/93 styrene/methyl methacrylate copolymer was 96 %, which is in good agreement with the anticipated results.

It appears, therefore, that the major constituent in a copolymer plays a pre-dominant part in the depolymerisation behaviour of copolymers and the results obtained in this work by pyrolysis/GLC (Table III) could be explained theoretically.

APPLICATIONS

A few selected examples are shown below:

Figs. 10–12 show the pyrograms of ethyl acrylate homopolymer and ethyl acrylate/methyl methacrylate copolymers 80/20 and 25/75, respectively. The traces were obtained by one shot pyrolysis at 450°, using a 4 m silicone oil column at 70°. Identical weights of polymer were depolymerised in each case (25 μg) and the instrument sensitivity was kept the same in all cases so as to permit a comparison of the amounts of various constituents evolved to be made. It may be seen that the ethyl acrylate monomer evolved by the 25/75 ethyl acrylate/methyl methacrylate copolymer is more than twice that evolved by the homopolymer although the amount of ethyl acrylate in the copolymer is one quarter that of the homopolymer. It may also be noticed that the amount of ethanol is considerably less in the 25/75 copolymer compared with the homopolymer.

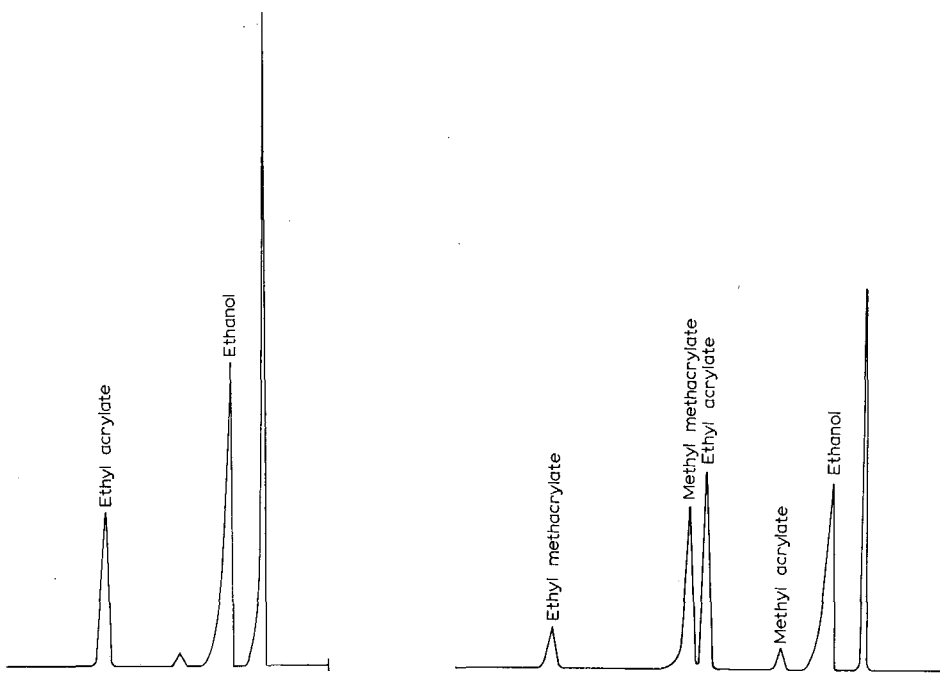Fig. 10. One shot pyrolysis at 450°; 4 m silicone oil column at 70°. Polyethyl acrylate, 25 μg.

Fig. 11. One shot pyrolysis and 450°; 4 m silicone oil column at 70°. Ethyl acrylate/methyl methacrylate copolymer (80/20), 25 μg.
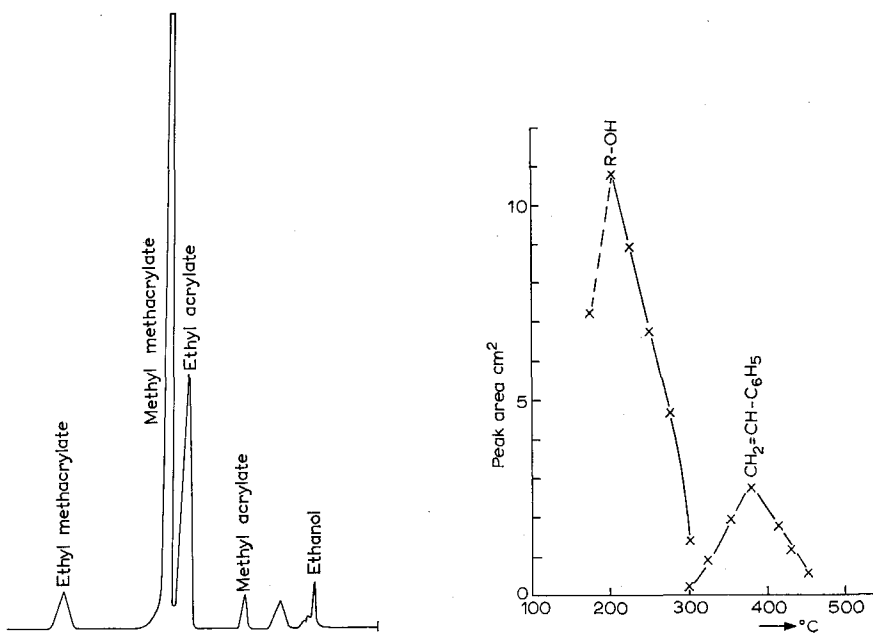
Fig. 12. One shot pyrolysis at 450°; 4 m silicone oil column at 70°. Ethyl acrylate/methyl methacrylate colpolymer (25/75), 25 μg.

Fig. 13. Stepwise depolymerisation of styrene/maleic monoalkyl ester.

Other noticeable points are the presence of methyl acrylate and ethyl meth-
acrylate in the breakdown products of the copolymer. Whether this ester interchange
takes place on depolymerisation or is effected in the initial copolymerisation is not
yet known.

Fig. 14. Stepwise depolymerisation of unknown samples. 1 = Styrene; 2 = methyl methacrylate;
3 = butyl acrylate; 4 = butyl methacrylate.

Fig. 13 shows the stepwise depolymerisation of a copolymeric styrene/maleic
acid monoalkyl ester. It indicates that the breakdown takes place in two stages:
First, elimination of the alcohol and the formation of anhydride. Secondly,

the breakdown of styrene/maleic anhydride copolymer.

Fig. 14 shows the stepwise depolymerisation of two unknown materials (A) and
(B). Both samples showed on one shot pyrolysis styrene, methyl methacrylate, butyl
acrylate and butyl methacrylate in various ratios. The stepwise depolymerisation, how-
ever, showed differences in styrene evolution which would indicate sample (A) to be a
random quadri-copolymer, whereas sample (B) is either a mixture of polystyrene and
quadri-copolymer or a block styrene copolymer with the quadri-copolymer.

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