Pyrolysis/gas chromatography/mass spectrometry of glycidyl methacrylate–alkyl acrylate copolymers

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Thermal degradation pattern of copolymers of glycidyl methacrylate with alkyl acrylates have been studied by pyrolysis/gas chromatography/mass spectrometry method. Various degradation products have been identified and based on the products obtained, the mechanisms of polymer degradation have been elucidated.

INTRODUCTION

Characterization of polymers by pyrolysis/gas chromatography/mass spectrometry (p/g.c./m.s.) has become a very useful tool for studying the thermal degradation of synthetic polymers[1]. This versatile technique is being used for the identification of degradation products of synthetic polymers enabling us to understand the mechanism of degradation of macromolecules under different conditions and to look for high temperature resistant and inflammable plastic materials[2,3]. Typical applications of this technique thus include structural identification of polymers, differentiation of isomeric structures, copolymer composition and average sequence length, identification of oligomers formed in the polymerization reaction and identification of volatile additives contained in polymer samples[4]. This technique can be applied to both soluble and insoluble polymers and direct pyrolysis in the mass spectrometer provides unique data with regard to the primary processes of thermal decomposition of polymers.

Glycidyl methacrylate (GMA) based copolymers have achieved potential applications in biology for the immobilization of biologically active species and in electronic industries as novel candidates for electron beam resists[5–7]. In our earlier articles[8,9], we reported copolymerization behaviour of this novel monomer (GMA) with various alkyl acrylates. This report is concerned with the elucidation of mechanisms of thermal degradation of some copolymers of GMA with alkyl acrylates with the aid of p/g.c./m.s. technique.

EXPERIMENTAL

Copolymers used for this study are GMA-Co-n-butyl acrylate (nBA), GMA-Co-isobutyl acrylate (iBA) and GMA-Co-tert. butyl acrylate (tBA) polymers. All these copolymers were synthesized in this laboratory by free radical copolymerization method and the details of synthesis have been dealt elsewhere[8].

Thermogravimetric analysis (t.g.a.) of the copolymers was performed with DuPont 900 thermal analyser at a heating rate of $10°C min^{-1}$ in nitrogen atmosphere.

Pyrolysis was carried out using a Philips Curie point pyrolyser; Curie point of the ferromagnetic sample probe being 610°C. The polymer from a solution in chloroform was deposited on the ferromagnetic wire. The amount of polymer deposited was about 10–15 mg in each case. The coated wires were stored for 24 h to allow evaporation of the solvent and the coated wire was mounted at the pyrolysis head. The probe heating rate and the duration of pyrolysis were preset and were highly reproducible. The head of the pyrolyser was interfaced with the gas chromatograph to trap the degradable products automatically. The gas chromatograph used was a Varian Instrument model 3700 with an injection needle insert adapted for pyrolysis unit. The column used was a Chromosorb 102 porous polymer column (60/80 mesh, $6' \times \frac{1}{8}''$ o.d.). The temperature of the column was 200°C and the helium carrier gas flow rate was $2 ml min^{-1}$. The pyrolysed products were detected by flame ionization.

The eluted pyrolysis peaks were identified by a Hewlett–Packard model 5985 A mass spectrometer coupled with a 5840 A gas chromatograph by a jet separator for the packed column. For this part of the study, only total ion chromatograms were collected using the mass spectrometer as the sole detector. This ensured optimal transfer of pyrolyzates to the ion source of the mass spectrometer. The electron impact ionization source was operated at an ionizing voltage of 70 eV, the ion source temperature being 200°C. A Hewlett–Packard model 2648 A data system was used to aid interpretation of mass spectra.

RESULTS AND DISCUSSION

Figure 1 shows the t.g.a. curves for GMA–nBA, GMA–iBA and GMA–tBA copolymers. The pyrograms of these copolymers are shown in *Figures 2–4* and the products thus obtained and identified are summarized in *Tables 1–3*.
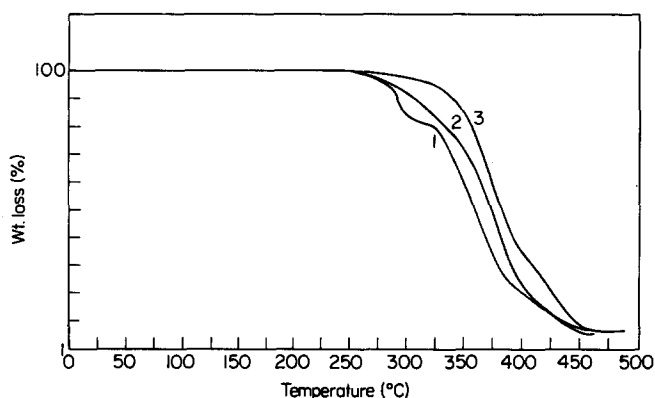
Figure 1 Thermogravimetric analysis of GMA-alkyl acrylate copolymers. (1) GMA-tBA (66:34); (2) GMA-iBA (65:35); (3) GMA-nBA (68:32)
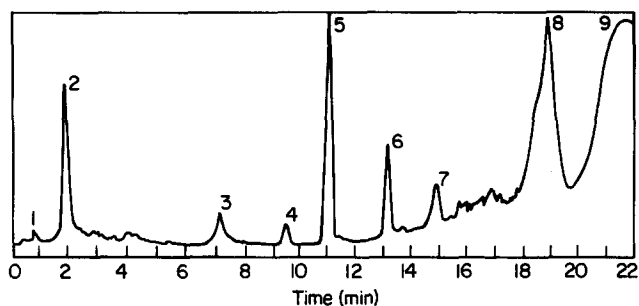

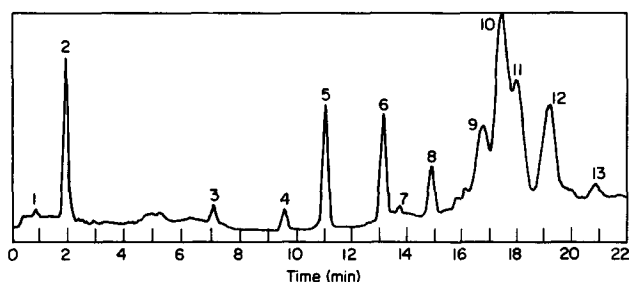**Figure 2** Pyrogram of GMA-nBA (68:32) copolymer

Figure 3 Pyrogram of GMA-iBA (65:35) copolymer

The thermograms indicate in all but GMA–tBA copolymer one stage weight loss. In the later case, the first stage weight loss is attributed to facile elimination of olefin, which is explained subsequently in this article. However, the t.g.a. involves slow heating while pyrolysis is a rapid process and the decomposition takes place in a short span of time.

Flash pyrolysis at 610°C (followed by separation and identification) indicated that the copolymers decompose in a random fashion yielding a variety of products. From the pyrograms it is evident that the degradation pattern of all the copolymers are nearly similar. By and large they yielded similar type of products, although in each case slightly different ratios of products resulted. Excepting few cases, the mechanisms of formation of most of the products have been suggested.

Liberation of butene and carbon dioxide

All the copolymers gave carbon dioxide and the corresponding butene due to the degradation of side chain ester group of butyl acrylate units. Initial step in the
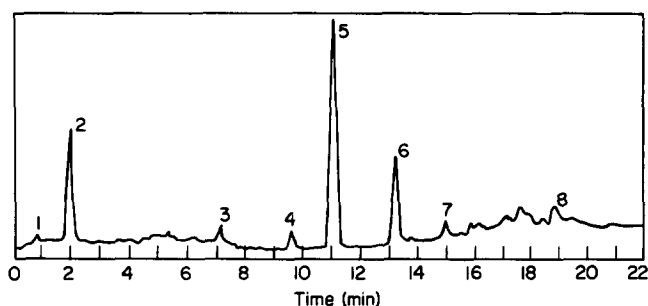

Figure 4 Pyrogram of GMA-tBA (66:34) copolymer

Table 1 Pyrolysed products of GMA–nBA (68:32) copolymer identified by g.c.–m.s.

Product	Ion mass
CO	28
CO_2	44
$CH_3-CH=CH_2$	42
CH_3-CHO	44
$CH_3-CH_2-CH=CH_2$	56
$CH_2=CH-CHO$	56
$CH_2=CH-CH_2OH$	58
$CH_2=\overset{\overset{CH_3}{\mid}}{\underset{\underset{COOCH_3}{\mid}}{C}}$	100

Table 2 Pyrolysed products of GMS–iBA (65:35) copolymer identified by g.c.–m.s.

Product	Ion mass
CO	28
CO_2	44
$CH_3-CH=CH_2$	42
CH_3-CHO	44
$CH_2=C\overset{CH_3}{\underset{CH_3}{<}}$	56
$CH_2=CH-CHO$	56
$CH_2=CH-CH_2-OH$	58
$CH=\overset{\overset{CH_3}{\mid}}{\underset{\underset{COOCH_3}{\mid}}{C}}$	100
$CH_3-CH_2-\overset{\underset{C=O}{\mid}}{CH_2}$ $O-CH_2-CH\overset{CH_3}{\underset{CH_3}{<}}$	144

Table 3 Pyrolysed products of GMA–tBA (66:34) copolymer identified by g.c.–m.s.

Product	Ion mass
CO	28
CO_2	44
$CH_3-CH=CH_2$	42
CH_3-CHO	44
$CH_2=C\overset{CH_3}{\underset{CH_3}{<}}$	56
$CH_2=CH-CHO$	56
$CH_2=CH-CH_2OH$	58

degradation of copolymers is likely to be scissoned at some unspecified point in the macromolecules. The reactive species generated in the first step would undergo subsequent reaction through a six membered transition state involving the carbonyl group and hydrogen atom on the β-carbon atom of the ester group yielding CO_2 and the corresponding olefin. The mechanism of this degradation process can be visualized as follows:

$R = R' = CH_3$, $R'' = R''' = H$, isobutyl
$R = R' = H$, $R'' = R''' = CH_3$, tert-butyl
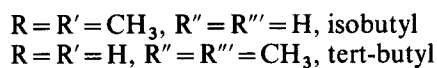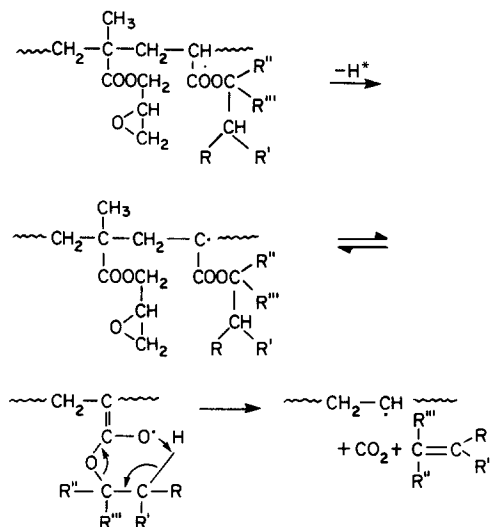
The formation of large quantity of butene in case of tBA containing copolymer (*Figures 2–4*) compared to nBA and iBA containing copolymers is due to the availability of larger number of β-hydrogen atoms (nine) in the case of former compared to one or two in case of the later copolymers[10]. Further, Grassie *et al.*[11,12] had reported the autocatalytic decomposition of the side chain ester group of poly-tert-butyl methacrylate due to a preformed acid. A similar type of mechanism might be operating in the case of GMA–tBA copolymer yielding larger amount of isobutene.
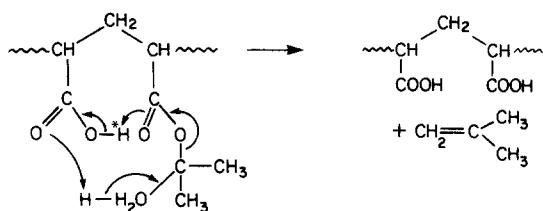
This is further substantiated by a two stage weight loss in this copolymer (*Figure 1*), the first weight being attributed to the facile elimination of isobutene.

Liberation of allyl alcohol, acrolein and acetaldehyde

All three copolymers yielded allyl alcohol, acrolein and acetaldehyde, suggesting these to be produced due to GMA moieties in the copolymers. The formation of these compounds have been assumed to be due to the decomposition of the ester group of GMA. The ester side chain decomposes to yield glycidyl radical which undergoes disproportionation with another glycidyl radical producing alcohol and aldehyde. The mechanism of these reactions can be visualized in the following manner.
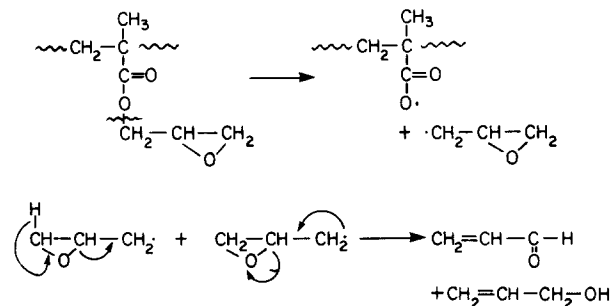
Similar types of reaction have been shown by McBay and Tuckers[13] between alkoxy radicals producing alcohol and aldehyde by disproportionation.

Similarly, liberation of epoxide radical produces acetaldehyde with abstraction of hydrogen atom.

$$CH_2-CH \xrightarrow{H\cdot} CH_3-CHO$$
$$\diagdown O \diagup$$
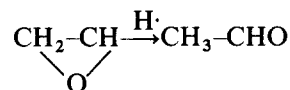
Other common products obtained were carbon monoxide and propene, which may be due to a certain type of degradation of side chain alkyl ester groups. In the case of iBA and nBA copolymers, formation of methyl methacrylate (*Tables 1* and *2*) may be due to the rearrangement of the side chain ester groups followed by main chain depolymerization in the following manner.
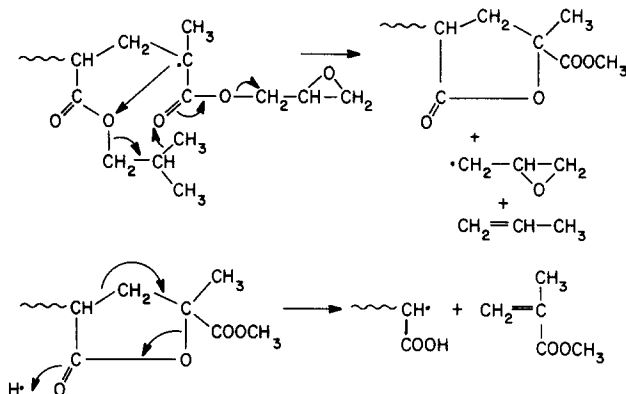
Surprisingly, no such product was observed in case of GMA–tBA copolymers. Moreover, the largest number of products (thirteen) were obtained during the decomposition of GMA–iBA copolymer, indicating various complicated modes of degradation of this material (*Table 2*).

CONCLUSION

In summary, it has been shown that pyrolysis of copolymers of GMA with various butyl acrylate monomers give a complex degradation pattern leading to the formation of variety of products. The degradation pattern is also influenced by the structure of side chain ester groups. Many of the products of degradation have been identified and finally plausible mechanisms for degradation, based on the pyrolysis products have been suggested.

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