

CHROM. 9379

QUANTITATIVE PYROLYSIS STUDIES OF STYRENE, ACRYLATE ESTER SYSTEMS, AND THEIR α -METHYL-SUBSTITUTED HOMOLOGS

J. K. HAKEN* and D. K. M. HO

Department of Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

SUMMARY

The pyrolytic degradation of copolymers and homopolymer mixtures of styrene, methyl acrylate, α -methylstyrene, and methyl methacrylate has been examined using a Curie Point pyrolysis system. The pyrolysis behaviour at several temperatures allows copolymers and mixtures to be distinguished. The essentially individual behaviour of homopolymers is observed and the concept of fragmentation indices as proposed for acrylic systems is considered.

INTRODUCTION

Pyrolysis gas chromatography of polymers has been the subject of many reports and has been described in a number of reviews¹⁻³. Much of the work has been of a qualitative nature and in many cases was conducted before the effects of the experimental and instrumental parameters had been evaluated. Large samples, *i.e.*, 2-15 mg, were frequently employed and with poor heat transfer and a preponderance of competing side reactions attempts at quantitation were of limited success.

The degradation mechanism of *n*-alkyl methacrylates with depropagation and depolymerisation with little accompanying transfer reaction is well established. The degradation of the *n*-alkyl acrylates is demonstrated by studies with polymethyl acrylate. Cameron and Kane^{4,5} proposed random initiation and a propagation step involving mainly transfer reactions with little depropagation. Subsequent analysis of the reaction products has substantiated these proposals⁶.

The early quantitative pyrolysis gas chromatographic studies of polyacrylic esters have been considered by McCormick⁷, who confirmed the observations of Strassburger *et al.*⁸ and of Gatrell and Mao⁹ that the yield of an acrylate monomer is substantially increased when pyrolysis of a copolymer containing a polymethacrylate is carried out as compared to pyrolysis of a homopolymer or of mixtures containing polyacrylate homopolymer. The ability of distinguishing between a copolymer and a mixture of homopolymers was demonstrated and the possibility of determining

* Temporary address until February 1977: Chemistry Department, Kent State University, Kent, Ohio 44242, U.S.A.

polymer composition suggested. Pyrolysis employed a helical filament with single shot or stepwise degradation with five polymer systems, *i.e.*, ethyl acrylate-methyl methacrylate, ethyl acrylate-*n*-butyl methacrylate, 2-ethylhexyl acrylate-methyl methacrylate, *n*-butyl acrylate-methyl methacrylate, and *n*-butyl methacrylate-methyl methacrylate.

The difficulties of calculating the pyrolysis yields with stepwise degradation at increasing temperatures were eliminated by the use of a radio frequency pyrolyser with several samples on elements of different Curie temperatures¹⁰. Copolymers and homopolymer mixtures of methyl to *n*-hexyl acrylate and methacrylate were studied. A constant fractional recovery of methacrylate monomer was achieved with homopolymers, copolymers, or a mixture containing polyalkyl methacrylates, while with polyacrylates the monomer yields were dependent on the presence of the esters in copolymers or homopolymers and in addition in a copolymer the yield of monomer decreased slightly as the percentage of acrylate was increased. The variations at the temperature used were relatively minor and the use of monomer yield allowed constants described as Homopolymer Fragmentation Indices (HFI) or Copolymer Fragmentation Indices (CFI) to be established and the composition of unknown copolymers or mixtures of homopolymers to be determined from pyrolysis data. The variation of the CFI values of the polyacrylates introduced only minor errors in the calculation of copolymer composition, the effect being most significant with copolymers of very high or very low acrylate content.

The present work examines the utility of these indices with several other polymers, namely, styrene, where thermal degradation occurs by a complex series of reactions which produce both monomer and transfer reaction products^{11,12}, and with α -methylstyrene, where depolymerisation predominates with high yields of monomer¹³⁻¹⁵. In this work copolymers and homopolymer mixtures of these monomers have been considered together and in combination with methyl acrylate and methyl methacrylate.

EXPERIMENTAL

Gas chromatography

Gas chromatography was conducted on a modified F & M Model 810/29 dual-column research chromatograph with flame ionization detection and fitted with an improved flow control system and on a Hewlett-Packard Model 5750 instrument. Two 12 ft. \times 1/4-in. O.D. aluminium columns packed with 10% OV-1 on 60-80 mesh Chromosorb W were programmed between 100 and 220° at 10°/min with the top temperature held for 5 min before automatic recycling occurred. Helium was used as the carrier gas at 40 ml/min. The amplifier sensitivity used generally was 16×10^2 A.f.s.d. and 2×10^2 A.f.s.d. for minor components.

Radiofrequency pyrolysis

A Philips Curie Point pyrolyzer was used. The ferromagnetic sample probes were prepared by forming a flat surface with light hammering for lengths of 1 cm at the end of the wires and then folding back these prepared tips to form a closed loop.

Solutions of the polymers were prepared and $0.50 \pm 0.2 \mu\text{l}$ of solution was deposited on wires with Curie Points of 510, 610, 770, and 980°. The amount of poly-

methyl methacrylate deposited was $10 \pm 0.4 \mu\text{g}$ and the approximate film thickness was calculated to be $0.5 \mu\text{m}$.

The coated wires were stored for 24 h to allow evaporation of solvent and the residual material was removed by allowing several minutes to elapse after mounting in the pyrolysis head prior to firing.

Polymer and copolymer preparation

Five sets of copolymers were prepared by free radical polymerisation using styrene- α -methylstyrene, styrene-methyl methacrylate, styrene-methyl acrylate, α -methylstyrene-methyl acrylate, and α -methylstyrene-methyl methacrylate. With each series five ratios were prepared, homopolymer mixtures of the same compositions were prepared from polymers free radical initiated, with the exception of α -methylstyrene, which employed an ionic initiator (concentrated sulphuric acid) at a low temperature (-50°).

RESULTS AND DISCUSSION

Pyrolyses of the homopolymers have been carried out at four temperatures, namely 510, 610, 770, and 980° and the monomer yields are shown in Table I.

TABLE I

MONOMER YIELDS FROM HOMOPOLYMERS WITH CURIE POINT PYROLYSIS

| Compound | 510° | 610° | 770° | 980° |
|--------------------------------|------|------|------|------|
| Methyl acrylate | 2.1 | 8.0 | 8.8 | 9.5 |
| Polystyrene | 5.0 | 71.6 | 74.8 | 75.3 |
| Polymethyl methacrylate | 76.3 | 98.6 | 97.4 | 96.6 |
| Poly(α -methylstyrene) | 91.0 | 98.0 | 98.0 | 98.0 |

Polymethyl acrylate and polymethyl methacrylate have previously been considered at the first three temperatures¹⁰, and while the monomer yields with polymethyl acrylate are somewhat lower than previously reported¹⁰, the temperatures of the maximum yield are the same for both polymers, as in the earlier report.

Pyrolysis of homopolymer mixtures (6:4) of styrene and α -methylstyrene exhibited pyrolysis patterns of the individual homopolymers which were similar to those of a copolymer of the same composition, which however showed a distinctly larger styrene monomer peak. Quantitative recoveries of monomer are shown in Table II for the series styrene- α -methylstyrene.

The homopolymers in the mixtures exerted little influence on each other and behaved independently although the presence of α -methylstyrene in the copolymers increased the proportionate yield of styrene. As the α -methylstyrene content increased, the relative yield of styrene showed a continued minor increase. The presence of styrene, however, did not influence the essentially quantitative yield of α -methylstyrene at 610, 770, and 980° . At 510° the presence of styrene had a marked influence on the α -methylstyrene yield, which decreased with increasing styrene content.

The proportionate monomer recoveries at 770° are shown in Figs. 1a and b for styrene and α -methylstyrene, respectively. Plots of the molar ratio of polymer and of

TABLE II
 PYROLYSIS YIELDS AT 510°, 610°, 770°, AND 980° FOR COPOLYMERS AND HOMOPOLYMER MIXTURES

| Relative ratios | | Percentage yield at 510° | | | | Percentage yield at 610° | | | | Percentage yield at 770° | | | | Percentage yield at 980° | | | |
|----------------------------|----------------|--------------------------|----------------|----------------|----------------|--------------------------|----------------|----------------|----------------|--------------------------|----------------|----------------|----------------|--------------------------|----------------|----------------|----------------|
| M ₁ | M ₂ | Copolymer | | Homopolymer | | Copolymer | | Homopolymer | | Copolymer | | Homopolymer | | Copolymer | | Homopolymer | |
| | | M ₁ | M ₂ | M ₁ | M ₂ | M ₁ | M ₂ | M ₁ | M ₂ | M ₁ | M ₂ | M ₁ | M ₂ | M ₁ | M ₂ | M ₁ | M ₂ |
| Styrene | | | | | | | | | | | | | | | | | |
| α-Methyl styrene | | | | | | | | | | | | | | | | | |
| 9 | 1 | 12.0 | 21.2 | 4.2 | 90.7 | 76.5 | 94.1 | 63.2 | 96.8 | 77.4 | 95.9 | 75.9 | 96.9 | 75.8 | 94.8 | 95.3 | 96.8 |
| 7 | 3 | 38.0 | 99.6 | 4.5 | 91.7 | 86.8 | 94.3 | 63.3 | 97.5 | 88.0 | 96.3 | 76.0 | 97.5 | 85.0 | 94.5 | 74.6 | 97.5 |
| 6 | 4 | 61.7 | 67.6 | 4.7 | 92.1 | 90.3 | 95.8 | 63.5 | 97.8 | 91.8 | 97.1 | 75.5 | 97.5 | 88.8 | 95.2 | 75.6 | 97.5 |
| 4 | 6 | 74.8 | 74.3 | 5.0 | 92.5 | 96.6 | 96.0 | 63.2 | 98.7 | 97.0 | 98.0 | 75.9 | 98.5 | 98.1 | 95.4 | 75.1 | 98.7 |
| 3 | 7 | 75.8 | 80.5 | 9.8 | 92.7 | 96.7 | 98.6 | 63.0 | 98.7 | 97.0 | 98.8 | 76.1 | 98.5 | 96.2 | 98.0 | 76.0 | 98.8 |
| Styrene | | | | | | | | | | | | | | | | | |
| Methyl methacrylate | | | | | | | | | | | | | | | | | |
| 9 | 1 | 6.8 | 24.6 | 5.0 | 76.3 | 77.1 | 78.7 | 64.9 | 96.6 | 79.0 | 88.6 | 73.8 | 94.1 | 78.4 | 84.4 | 72.5 | 93.6 |
| 7 | 3 | 10.1 | 33.4 | 5.2 | 73.4 | 82.4 | 84.3 | 66.2 | 95.6 | 89.4 | 91.0 | 73.8 | 94.7 | 87.8 | 87.7 | 72.8 | 93.8 |
| 5 | 5 | 31.6 | 40.2 | 10.8 | 75.9 | 87.8 | 89.3 | 64.9 | 95.6 | 93.8 | 93.8 | 73.8 | 95.1 | 92.3 | 91.0 | 72.8 | 94.0 |
| 3 | 7 | 58.5 | 60.2 | 5.7 | 73.4 | 93.5 | 93.7 | 65.3 | 96.6 | 94.4 | 94.5 | 73.8 | 95.5 | 93.6 | 93.0 | 72.9 | 95.0 |
| 1 | 9 | 74.0 | 71.6 | 8.0 | 76.0 | 94.4 | 94.1 | 65.8 | 96.8 | 95.0 | 95.0 | 73.8 | 95.8 | 94.5 | 93.2 | 72.8 | 95.1 |
| Styrene | | | | | | | | | | | | | | | | | |
| Methyl acrylate | | | | | | | | | | | | | | | | | |
| 9 | 1 | 6.7 | 2.3 | 6.7 | 2.2 | 61.0 | 38.6 | 65.1 | 8.1 | 69.3 | 47.3 | 75.5 | 8.8 | 69.7 | 48.2 | 75.3 | 9.5 |
| 7 | 3 | 4.9 | 2.0 | 5.0 | 2.4 | 44.1 | 33.3 | 65.2 | 8.2 | 59.4 | 40.2 | 75.0 | 8.7 | 60.5 | 41.0 | 75.3 | 9.5 |
| 5 | 5 | 5.0 | 2.8 | 5.0 | 2.2 | 42.9 | 28.9 | 63.8 | 8.0 | 49.0 | 34.1 | 75.2 | 8.8 | 51.2 | 35.3 | 75.3 | 9.4 |
| 3 | 7 | 5.0 | 2.0 | 6.0 | 2.1 | 31.6 | 14.0 | 63.9 | 7.9 | 38.6 | 17.3 | 75.2 | 8.7 | 40.4 | 17.7 | 75.3 | 9.4 |
| 1 | 9 | 4.9 | 2.0 | 6.0 | 2.1 | 29.1 | 9.8 | 63.5 | 7.3 | 31.5 | 11.5 | 75.3 | 8.8 | 32.8 | 12.1 | 75.3 | 9.4 |
| α-Methyl styrene | | | | | | | | | | | | | | | | | |
| Methyl methacrylate | | | | | | | | | | | | | | | | | |
| 7 | 3 | 92.3 | 79.4 | 91.6 | 78.2 | 98.5 | 96.2 | 98.3 | 98.6 | 98.5 | 97.0 | 98.3 | 97.4 | 98.5 | 98.7 | 98.3 | 97.0 |
| 6 | 4 | 91.7 | 80.2 | 91.2 | 78.8 | 98.5 | 95.3 | 98.0 | 98.5 | 98.5 | 96.2 | 98.0 | 97.6 | 98.6 | 98.0 | 98.0 | 97.1 |
| 4 | 6 | 92.0 | 81.0 | 91.0 | 78.5 | 98.4 | 96.8 | 98.2 | 98.6 | 98.4 | 97.2 | 98.2 | 97.2 | 98.6 | 98.4 | 98.2 | 96.9 |
| 3 | 7 | 92.0 | 78.8 | 91.1 | 78.5 | 98.2 | 97.1 | 98.0 | 98.5 | 98.4 | 97.6 | 98.0 | 97.8 | 98.4 | 98.2 | 98.0 | 97.0 |
| 1 | 9 | 91.5 | 80.1 | 91.4 | 78.7 | 98.0 | 97.2 | 98.2 | 98.2 | 98.1 | 97.8 | 98.2 | 97.3 | 98.4 | 98.3 | 98.2 | 96.8 |
| α-Methyl styrene | | | | | | | | | | | | | | | | | |
| Methyl acrylate | | | | | | | | | | | | | | | | | |
| 9 | 1 | 79.8 | 36.6 | 90.6 | 2.1 | 96.3 | 48.8 | 98.2 | 7.4 | 98.0 | 50.1 | 98.2 | 8.8 | 97.4 | 49.1 | 98.2 | 9.5 |
| 1 | 1 | 75.8 | 30.1 | 92.0 | 2.0 | 96.5 | 45.3 | 98.0 | 7.2 | 98.2 | 48.7 | 98.0 | 8.5 | 97.5 | 45.6 | 98.0 | 9.2 |
| 4 | 6 | 73.4 | 28.0 | 71.0 | 2.1 | 97.3 | 43.4 | 98.0 | 7.4 | 98.0 | 46.2 | 98.0 | 8.7 | 98.0 | 44.2 | 98.0 | 9.5 |
| 3 | 7 | 92.2 | 5.8 | 91.4 | 2.2 | 95.8 | 16.4 | 98.0 | 7.2 | 98.0 | 17.2 | 98.0 | 8.6 | 98.0 | 17.0 | 98.0 | 9.3 |
| 1 | 9 | 24.0 | 3.4 | 71.3 | 2.3 | 96.0 | 10.0 | 97.8 | 7.5 | 98.0 | 10.9 | 98.0 | 8.8 | 98.0 | 10.9 | 98.0 | 9.5 |

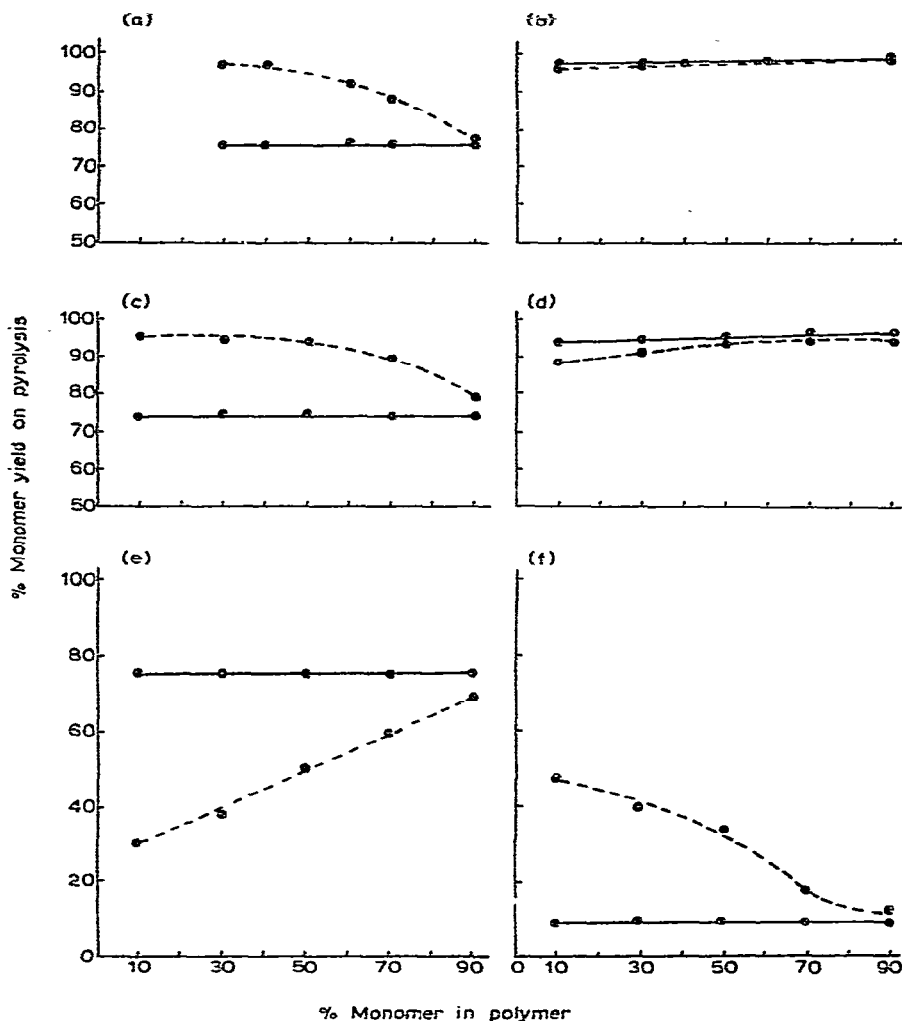


Fig. 1. Plots showing proportionate monomer recoveries for copolymer and homopolymer mixtures of: (a) styrene, (b) α -methylstyrene, (c) styrene, (d) methyl methacrylate, (e) styrene, and (f) methyl acrylate. ---, Copolymer; —, polymer mixture.

pyrolysis products are shown in Fig. 2a, where it is apparent that essentially linear relationships exist, the copolymer plot being uppermost due to the greater styrene yields and the higher styrene/ α -methylstyrene ratio.

By considering pyrolysis at various temperatures, it was possible to differentiate between copolymers and polymer mixtures. With mixtures α -methylstyrene showed maximum recoveries at 610°, 770°, and 980°, while styrene showed maxima at 770° and 980°. In copolymers, both monomers showed the greatest yields at 770°. The effects with systems of 6:4 monomer ratios are shown in Fig. 3.

CFI and HFI values were determined for all samples at 770° and are shown in Table III. It is apparent that the CFI and HFI values for α -methylstyrene show

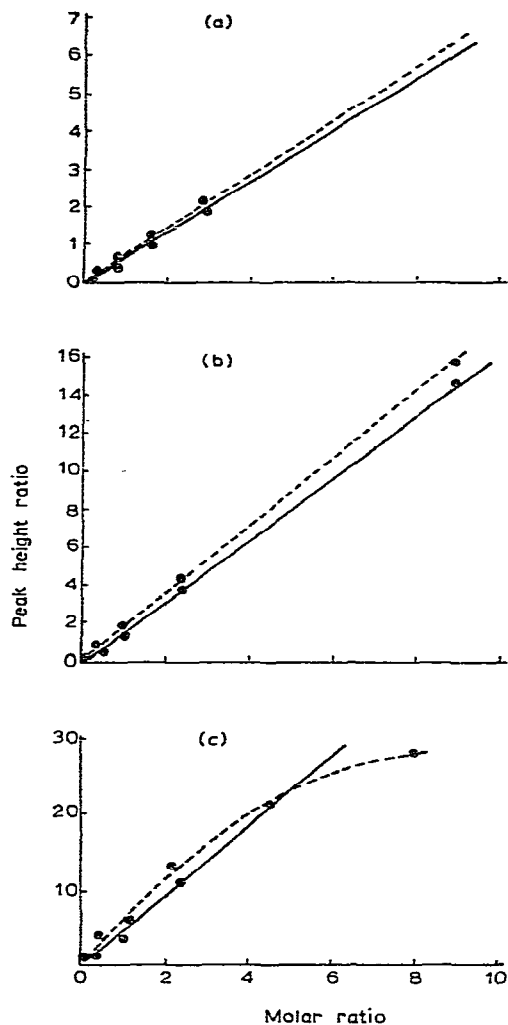


Fig. 2. Plots of percentage composition (peak height ratios) of polymers and of pyrolysis products for: (a) styrene- α -methylstyrene, (b) styrene-methyl methacrylate, and (c) styrene-methyl acrylate. ---, Copolymer; —, polymer mixture.

respective constancies, while with styrene the HFI values are constant but the CFI values show a variation according to the composition of the copolymer.

Quantitative yields of monomer from copolymers and homopolymers of styrene and methyl methacrylate are shown in Table II, the individual performance of the homopolymers in admixture being again evident while in the copolymers both styrene and methyl methacrylate yields were influenced by the presence of each other. In general, the styrene yield was increased with increased contents of methyl methacrylate while the methyl methacrylate yield showed a gradual decrease as the styrene concentration in the copolymer increased (Figs. 1c and d).

Maximum styrene monomer recovery was achieved at 770° for both copolymers

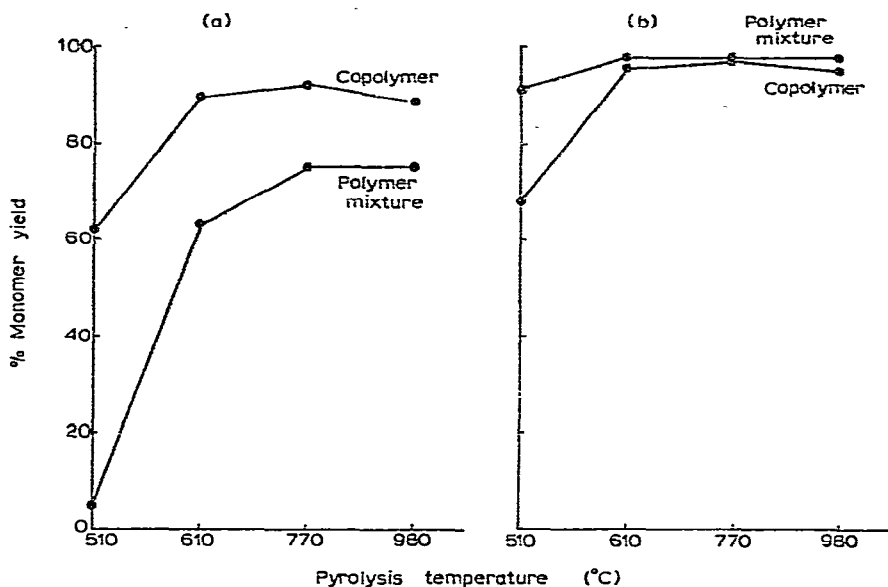


Fig. 3. Influence of pyrolysis temperature on monomer yields of: (a) styrene and (b) α -methylstyrene from copolymer and polymer mixtures.

and mixtures. By the use of the recovery of methyl methacrylate the sample could be identified as a mixture. With homopolymers the maximum ester yield was at 610° and in copolymers at 770°.

Molar ratio plots, *i.e.*, peak height ratios of pyrolysis products vs. molar ratios of polymers, for both copolymers and homopolymer mixtures exhibited linear relationships, as shown in Fig. 2b. The CFI and HFI values are shown in Table III and with both monomers the HFI values were constant while the CFI values again varied, slightly depending on the composition of the copolymer.

Both copolymers and homopolymer mixtures of styrene and methyl acrylate yielded complex pyrograms characteristic of those of the individual homopolymers.

Quantitative yields of monomer from copolymers and homopolymer blends are shown in Table II. The individual behaviour of the two monomers in homopolymer mixtures was again evident, however, with copolymers both styrene and methyl acrylate affected each other in monomer yields. When the styrene molar ratio was increased, the percentage recovery of both styrene and methyl acrylate increased accordingly, and when the molar ratio of methyl acrylate was increased, the percentage recovery of both monomers decreased. The effect is shown in Figs. 1e and f and again in Fig. 3c, where the considerable variation in the molar ratios of the polymer and the pyrolysis products is evident from the lack of linearity of the copolymer plot. The HFI values for both monomers are constant and the CFI values greatly variant, as shown in Table III.

Yields of monomer from the series α -methylstyrene and methyl methacrylate are shown in Table II, while fragmentation indices are shown in Table III, where it is evident that both these monomers, which degrade by depolymerisation, are virtually unaffected by the presence of the comonomer.

TABLE III
COPOLYMER AND HOMOPOLYMER FRAGMENTATION INDICES AT 770°

| | <i>Styrene</i> | | <i>α-Methylstyrene</i> | | <i>α-Methylstyrene</i> | | <i>Methyl methacrylate</i> | |
|-----|----------------|------------|----------------------------|------------|------------------------|------------|----------------------------|------------|
| | <i>CFI</i> | <i>HFI</i> | <i>CFI</i> | <i>HFI</i> | <i>CFI</i> | <i>HFI</i> | <i>CFI</i> | <i>HFI</i> |
| 1 | 1.29 | 1.32 | 1.03 | 1.03 | 1.02 | 1.02 | 1.03 | 1.03 |
| 2 | 1.14 | 1.32 | 1.04 | 1.03 | 1.02 | 1.02 | 1.04 | 1.02 |
| 3 | 1.09 | 1.32 | 1.02 | 1.02 | 1.02 | 1.02 | 1.03 | 1.03 |
| 4 | 1.03 | 1.32 | 1.06 | 1.01 | 1.02 | 1.02 | 1.02 | 1.02 |
| 5 | 1.03 | 1.32 | 1.01 | 1.02 | 1.02 | 1.02 | 1.02 | 1.03 |
| Av. | 1.12 | 1.32 | 1.03 | 1.03 | 1.02 | 1.02 | 1.03 | 1.03 |
| | <i>Styrene</i> | | <i>Methyl methacrylate</i> | | <i>α-Methylstyrene</i> | | <i>Methyl acrylate</i> | |
| | <i>CFI</i> | <i>HFI</i> | <i>CFI</i> | <i>HFI</i> | <i>CFI</i> | <i>HFI</i> | <i>CFI</i> | <i>HFI</i> |
| 1 | 1.27 | 1.35 | 1.13 | 1.06 | 1.02 | 1.04 | 2.00 | 11.40 |
| 2 | 1.12 | 1.32 | 1.10 | 1.06 | 1.02 | 1.02 | 2.06 | 11.59 |
| 3 | 1.06 | 1.32 | 1.07 | 1.05 | 1.02 | 1.02 | 2.16 | 11.39 |
| 4 | 1.05 | 1.33 | 1.06 | 1.06 | 1.02 | 1.02 | 5.79 | 11.62 |
| 5 | 1.04 | 1.32 | 1.05 | 1.05 | 1.03 | 1.02 | 9.20 | 11.38 |
| Av. | 1.11 | 1.33 | 1.08 | 1.06 | 1.02 | 1.02 | 4.24 | 11.48 |
| | <i>Styrene</i> | | <i>Methyl acrylate</i> | | | | | |
| | <i>CFI</i> | <i>HFI</i> | <i>CFI</i> | <i>HFI</i> | | | | |
| 1 | 1.44 | 1.32 | 2.12 | 11.40 | | | | |
| 2 | 1.65 | 1.33 | 2.49 | 11.55 | | | | |
| 3 | 2.02 | 1.31 | 2.94 | 11.26 | | | | |
| 4 | 2.47 | 1.32 | 5.77 | 11.34 | | | | |
| 5 | 3.19 | 1.32 | 8.67 | 11.32 | | | | |
| Av. | 2.15 | 1.32 | 4.40 | 11.37 | | | | |

When methyl acrylate is replaced by methyl methacrylate the monomer yields are significantly altered (Table II), as shown by plots of peak height ratios and composition.

The CFI and HFI values for α -methylstyrene are essentially identical, although with methyl acrylate the values are widely variant, higher yields of methyl acrylate from copolymers being evident by the lower CFI values, as shown in Table III.

From Table III it is apparent that the average values of the fragmentation indices for a particular monomer are very similar when in combination with any of the three comonomers, the exception being with styrene when copolymerised with methyl acrylate, where increased methyl acrylate in the copolymers leads to decreased styrene recovery.

The linearity of the plots of the molar ratio of the pyrolysis products and the copolymer composition for styrene with α -methylstyrene and with methyl methacrylate is in agreement with the work of Strassburger *et al.*⁸ and that of Ferlanto *et al.*¹⁶, who considered copolymers of methyl methacrylate with methyl and ethyl

acrylate, respectively. In all of these examples one of the monomers is substantially depolymerised while the other is subjected to significant degradation. In this work the system styrene-methyl acrylate is anomalous as both of the monomers are subject to substantial degradation. The individual behaviour of homopolymers in mixtures is in agreement with earlier works^{8,9}, with the exception that Ferlanto *et al.*¹⁶ reported a concentration dependence. In the absence of data, it is not possible to consider the degree of this dependence. From the systems studied it is evident that homopolymer mixtures are of limited value for use as compositional models for pyrolysis studies of copolymer systems.

The acrylate-methacrylate system has been discussed^{10,16} and while random polymerisation is involved, the product is considered analogous to a block copolymer. The number of acrylate-methacrylate bonds tend to remain constant once the limiting number of these bonds are formed and these rather than the size of the acrylate block determine the pyrolysis yield of acrylate monomer. To further investigate this hypothesis Ferlanto *et al.* employed the sequence distribution of Harwood *et al.*¹⁷ to determine the number of acrylate-methacrylate bonds. Some support was obtained with low-conversion copolymers but with high-conversion copolymers considerable discrepancies were evident. The variation between calculations with high- and low-conversion copolymers is not unexpected due to the limitations of the copolymer composition equation with increasing conversion.

REFERENCES

- 1 M. P. Stevens, *Characterization and Analysis of Polymers by Gas Chromatography*, Marcel Dekker, New York, 1969.
- 2 G. M. Brauer, in P. E. Slade, Jr. and L. T. Jenkins (Editors), *Thermal Characterization Techniques*, Marcel Dekker, New York, 1970.
- 3 J. K. Haken, *Gas Chromatography of Coating Materials*, Marcel Dekker, New York, 1974.
- 4 G. G. Cameron and D. R. Kane, *Makromol. Chem.*, 109 (1967) 194.
- 5 G. G. Cameron and D. R. Kane, *J. Polym. Sci., Part B*, 2 (1964) 693.
- 6 J. K. Haken and D. K. M. Ho, *J. Polym. Sci., Polym. Chem. Ed.*, 12 (1974) 1163.
- 7 H. McCormick, *J. Chromatogr.*, 4C (1969) 1.
- 8 J. Strassburger, G. M. Brauer, M. Tyron and A. F. Forziati, *Anal. Chem.*, 32 (1960) 454.
- 9 R. L. Gatrell and T. J. Mao, *Anal. Chem.*, 37 (1965) 1294.
- 10 J. K. Haken and T. R. McKay, *Anal. Chem.*, 45 (1973) 1251.
- 11 S. L. Madorsky and S. Straus, *J. Res. Nat. Bur. Stand.*, 40 (1948) 417.
- 12 P. Bradt, V. H. Dibeler and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, 50 (1953) 201.
- 13 W. S. Reid, *J. Soc. Chem. Ind.*, 68 (1949) 244.
- 14 S. Straus and S. L. Madorsky, *J. Res. Nat. Bur. Stand.*, 50 (1953) 165.
- 15 S. Straus and S. L. Madorsky, *J. Res. Nat. Bur. Stand., Sect. A*, 66 (1962) 401.
- 16 E. C. Ferlanto, M. K. Lindemann, C. A. Lucchesi and D. R. Gaskell, *J. Appl. Polym. Sci.*, 15 (1971) 445.
- 17 J. H. Harwood, N. W. Johnston and H. Piotrowski, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 8 (1967) 199.