

## Pyrolysis of Poly(methyl Methacrylate *co* Ethyl Acrylate)

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### Synopsis

An investigation of the behavior of poly(methyl methacrylate *co* ethyl acrylate) with a commercially available filament-type pyrolysis unit and gas chromatograph was conducted. It has been hypothesized that the quantity of ethyl acrylate monomer produced under the conditions of the experiment is dependent upon the number of ethyl acrylate-methyl methacrylate bonds contained in the copolymer. These observations were made possible by a standardized samples-handling technique in which a uniform-size disk was pyrolyzed at a maximum pyrolysis temperature of 600°C. This enabled reproducible pyrolysis gas chromatograms to be obtained and permitted pyrolysis products of copolymers containing different ratios of ethyl acrylate and methyl methacrylate to be compared. An examination of sequence distribution data, obtained with the aid of a sequence distribution program for copolymers, showed sufficient agreement with the pyrolysis data to support the hypothesis. It has been demonstrated that pyrolysis gas chromatography may be applied to experimentally determine the sequence distribution of copolymers.

### INTRODUCTION

The characterization of copolymer materials is necessary for the development of new materials and the control of commercial processes. Acrylic copolymers are of current commercial interest for the formulation of many coating materials such as coil coatings and automotive coatings. The characterization of copolymer materials may employ analytical techniques such as infrared spectroscopy, nuclear magnetic resonance spectroscopy, thermal studies, gel permeation chromatography, and pyrolysis gas chromatography.

The application of pyrolysis gas chromatography as a characterization technique is similar in principle to the study of fragmentation patterns with mass spectrometry. In both processes, energy is employed to fragment a molecule and results in a fragmentation pattern which is identifiable and unique for a particular compound. Pyrolysis gas chromatography has not been as thoroughly studied as mass spectrometry, but it is a technique

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which must be seriously considered for the study of organic compounds that are nonvolatile and complex in structure.

Haslam and Jeffs<sup>1</sup> and Radell and Strutz<sup>2</sup> were among the early workers who investigated the application of gas chromatography to the separation and identification of pyrolysis products. They demonstrated that gas chromatography coupled with a controlled temperature pyrolysis technique can be employed as a rapid semiquantitative method for the determination of the composition of mechanical mixtures of acrylic and methacrylic polymers.

Later workers<sup>3-5</sup> found that the pyrolysis temperature influences the mode of degradation and affects the type and distribution of fragmentation products observed. Esposito<sup>6</sup> reported that acrylic polymers can be quantitatively analyzed if an internal standard is employed in conjunction with a special coating technique. It has been further reported<sup>7</sup> that copolymers containing methyl methacrylate could be distinguished from mechanical mixtures of analogous composition because the chromatograms of their pyrolysis products were not identical.

A recent paper by Levy<sup>8</sup> sought to define trends and performance requirements of pyrolysis units with a view toward interlaboratory use of pyrolysis gas chromatography reference data. Another recent study by Farré-Rius and Guiochon<sup>9</sup> indicated that with flash probe (pulse mode) pyrolysis, decomposition of microgram samples of polymer is determined by the heating rate of the filament and the rate of heat transfer to the sample, not by the equilibrium temperature of the filament.

The identification and semiquantitative analysis of homopolymers and mechanical mixtures of methacrylic polymers have been conducted successfully in this laboratory with a commercially available filament-type pyrolysis unit attached to a gas chromatograph. It was observed that the pyrolysis products of copolymer systems composed of ethyl acrylate and methyl methacrylate were inconsistent with the products obtained with mixtures of the homopolymers, an observation which is in agreement with those of other workers. An investigation was conducted to relate the composition of poly(methyl methacrylate *co* ethyl acrylate), a commercially important copolymer, to the products detected with pyrolysis gas chromatography.

In the course of this work, an observation was made regarding the mode of degradation of the copolymer. It was hypothesized that the amount of ethyl acrylate monomer produced is dependent upon the number of ethyl acrylate-methyl methacrylate bonds contained in the copolymer. An examination of sequence distribution data showed sufficient agreement with the pyrolysis data to support the hypothesis. It was also observed that semiquantitative analysis of this copolymer system could be conducted with pyrolysis gas chromatography. This is in agreement with reports of other investigators<sup>7</sup> who have shown that a plot of the ratio of the monomers detected with pyrolysis gas chromatography versus the copolymer composition yields a suitable calibration curve.

## EXPERIMENTAL

### Apparatus

An F&M Model 810 gas chromatograph was used with a Model 80 pyrolysis unit and an Infotronics Model CRS-11HS electronic integrator. Two columns were employed, a LAC-446 polyester (diethylene glycol adipate) with a 1% phosphoric acid column (6 ft  $\times$   $\frac{1}{4}$  in. OD) and a DC-11 silicone grease column (16 ft  $\times$   $\frac{1}{8}$  in. OD), both of which were operated isothermally at 75°C.

Also employed were a Hewlett Packard Probe Yoke 2-3411-1 and a Buehler Press Model 20-1311 equipped with a  $1\frac{1}{4}$ -in. cylinder.

### Synthesis of Reference Polymers and Copolymers

Homopolymers and copolymers of ethyl acrylate and methyl methacrylate were synthesized by bulk polymerization in dilatometer tubes. The reaction temperature was held at 60°C, and 0.1% benzoyl peroxide was employed as catalyst. Volume changes in the dilatometer tubes were measured as a means of following the course of the polymerizations and for calculating the percent conversion of total monomer. The dilatometer tubes were frozen in Dry Ice, the contents were diluted with acetone, and the polymer was precipitated twice from acetone solution with heptane. The precipitates were vacuum dried at 50°C for 24 hr. Two sets of copolymers were synthesized, one set representing low-conversion copolymers and the other representing high-conversion copolymers. The values of the reactivity ratios and the per cent conversions were used to calculate the theoretical compositions and sequence distributions of the resulting copolymers. The compositions are shown in Table I. The compositions of the low conversion copolymers were verified via the nuclear magnetic resonance spectroscopy method of Yeagle and Scott.<sup>10</sup> The NMR data are also presented in Table I.

### Sample Preparation

A 100-mg sample was weighed and placed between two Teflon or aluminum disks ( $1\frac{1}{4}$ -in. diameter) to protect the sample from contamination in the press. The sandwich was then placed on the cylinder of a Buehler press, the ram was set in place, and heat was applied until the temperature reached 150°C. A pressure of about 4200 lb was applied and held for about 1 min, and then the cylinder was allowed to cool. The protective disks were peeled from the sample to obtain the polymer film. A circle,  $\frac{1}{8}$  in. in diameter, was punched from the film for insertion into the pyrolysis probe.

A Model 2-3411-1 probe, available from Hewlett Packard Corporation, was employed; it contains a W-type rhodium-platinum filament. The sample was placed between the filament ends and held mechanically by exerting slight pressure on the tip of the filament. The probe containing

TABLE I  
Composition and Pyrolysis Gas Chromatography Data for Low-Conversion and High-Conversion Copolymers  
of Poly(methyl Methacrylate-co Ethyl Acrylate)<sup>a</sup>

Sample <sup>b</sup>	Composition from NMR EA/MMA	Composition computed EA/MMA	Monomer charge EA/MMA	Conversion, %	Peak area from pyrolysis gas chromatogram		Ratio of peak areas, EA counts/ MMA counts	Sequence distribution calculation of AB + BA fraction
					EA, counts (avg)	MMA, counts (avg)		
A. Low-Conversion Copolymers								
1	10/90	11/89	20/80	5.2	19,733	397,256	0.050	0.18
2	23/77	24/76	40/60	10.6	45,916	254,183	0.180	0.36
3	38/62	40/60	60/40	4.8	47,989	172,762	0.277	0.49
4	60/40	64/36	80/20	5.0	44,158	88,312	0.499	0.47
B. High-Conversion Copolymers								
5	n.d.	18/82	20/80	96.8	10,538	83,763	0.126	0.28
6	n.d.	39/61	40/60	98.8	16,985	96,504	0.176	0.42
7	n.d.	60/40	60/40	99.9	14,914	48,585	0.308	0.43
8	n.d.	80/20	80/20	99.6	12,069	20,620	0.575	0.30

<sup>a</sup> Methyl methacrylate reactivity ratio 2.21; ethyl acrylate reactivity ratio 0.41; n.d. means not determined.

<sup>b</sup> Experiments were conducted for the low-conversion and high-conversion copolymers with different probe filaments; therefore, a comparison of peak areas measured for low- and high-conversion copolymers cannot be made with the data presented here.

the sample to be pyrolyzed was placed in the injection port of the chromatograph (an adapter is provided for placing the probe assembly directly onto the injection port). The maximum temperature of pyrolysis was controlled by setting the current applied to the probe. Each probe is accompanied by a temperature-current calibration chart supplied by the manufacturer. The Model 80 pyrolysis unit is equipped with a 60-sec delay timer which is automatically switched to a timed (12-sec) pyrolysis.

The pyrolysis products were swept directly onto the chromatograph column by the helium carrier gas. The peak areas were measured with an electronic integrator; they were found to be reproducible for a given sample with a single pyrolysis probe unit but varied with different probes. The ratio of peak areas observed for ethyl acrylate and methyl methacrylate remained constant, within experimental error, even with different pyrolysis probe units.

### RESULTS AND DISCUSSION

The peak areas corresponding to the two major products of pyrolysis, ethyl acrylate (EA) and methyl methacrylate (MMA), were measured, and the ratio of the EA/MMA peak areas was plotted versus the copolymer composition in accordance with the technique of Strassburger and co-workers.<sup>7</sup> The data obtained with the DC-11 silicone grease column for the set of low-conversion copolymers yielded a straight-line plot which, by a linear regression calculation, can be represented by the equation

$$y = 120.8x + 4.37$$

where  $y$  is the % ethyl acrylate in the copolymer and  $x$  is the ratio of peak areas of EA to MMA.

A calibration curve was constructed in similar fashion for the high-conversion series of copolymers.

Eleven replicate pyrolysis determinations (for which the same probe was used) were obtained with copolymer 4 (see Table IA) to give a standard deviation of  $\pm 0.040$  for the EA/MMA peak area ratio. The 95% confidence interval calculation for this copolymer showed a 12.6% error in the determination of copolymer composition under these conditions.

It can be seen in Table IA that the average area of the EA monomer peak from the pyrolysis of each of the four low-conversion copolymers was relatively constant (from 24% to 64% ethyl acrylate content). The area of the MMA peak varied to give the linear relation between the EA/MMA peak area ratio and the weight per cent of the EA in the copolymer. It was expected that the area of each monomer peak would be a function of the concentration of the monomer in the copolymer. In an effort to understand these results, experiments were conducted with the homopolymers of each monomer in admixture with poly( $\alpha$ -methylstyrene) and with mixtures of the two homopolymers. The set of high-conversion copolymers showed a similar independence of ethyl acrylate monomer peak area versus its concentration in the copolymer (Table IB). Experiments were conducted

TABLE II  
Ethyl Acrylate Peak Areas Produced in the Pyrolysis of Poly(ethyl Acrylate) Mixed  
with Poly( $\alpha$ -methylstyrene)

Sample	EA counts	Poly(ethyl acrylate) in mixture with poly( $\alpha$ -methylstyrene), mole-%
A	not detected	15
B	7,100	40
C	14,500	67
D	21,500	85

for the low-conversion copolymers and high-conversion copolymers with different probe filaments. Therefore, a comparison of peak areas measured for low- and high-conversion copolymers cannot be made with the data presented here.

The area of the EA monomer peak produced during the pyrolysis of mixtures of ethyl acrylate homopolymer and poly( $\alpha$ -methylstyrene) showed a dependence on the concentration of ethyl acrylate in the polymer mixture, as can be seen in Table II. Since all of the samples tested were  $1/8$ -in. disks punched from films pressed with 100 mg of material, the ethyl acrylate content was nominally the same in the mixtures and the copolymers in the range tested.

Pyrolysis of mixtures of the two homopolymers, poly(ethyl acrylate) and poly(methyl methacrylate), having compositions analogous to the copolymers, also showed that the peak area of each monomer was concentration dependent for the mixtures.

An investigation was conducted to determine the relative peak areas of products (other than hydrocarbons) for each of the low-conversion copolymers. A LAC-446 polyester + 1% phosphoric acid column operated at 75°C was employed for these determinations. This column does not resolve the ethyl acrylate and methyl methacrylate peaks; therefore, the sum of the peak areas for these monomers was calculated. It was observed that the decomposition products, identified by virtue of their retention times, varied in a consistent manner with changes in the composition of the copolymer. The decomposition products were identified as methyl alcohol, ethyl alcohol, and methyl acrylate, as well as ethyl acrylate and methyl methacrylate. The plot of the relative amounts of these decomposition products versus copolymer composition are shown in Figures 1 and 2.

The consistency of the changes observed in the amounts of decomposition products with changes in the copolymer composition reflects the quantitative nature and reproducibility of the technique adopted to obtain pyrolysis gas chromatograms.

The trend toward constant average peak area of ethyl acrylate monomer (above 24% by weight of ethyl acrylate in the copolymer), as determined with the DC-11 silicone grease column, suggests that a control factor has been introduced into the copolymer structure which influences the degree

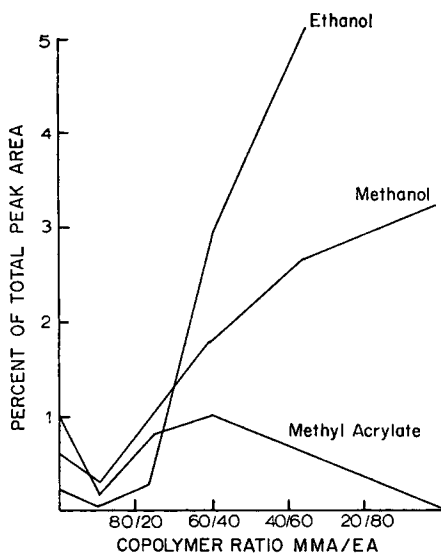


Fig. 1. Composition of pyrolysis products vs. copolymer composition.

to which this pyrolysis product is formed. A limitation upon the number of EA-MMA bonds formed may exist due to the greater reactivity ratio of methyl methacrylate (2.21) compared with ethyl acrylate (0.41) and may provide such a control factor.

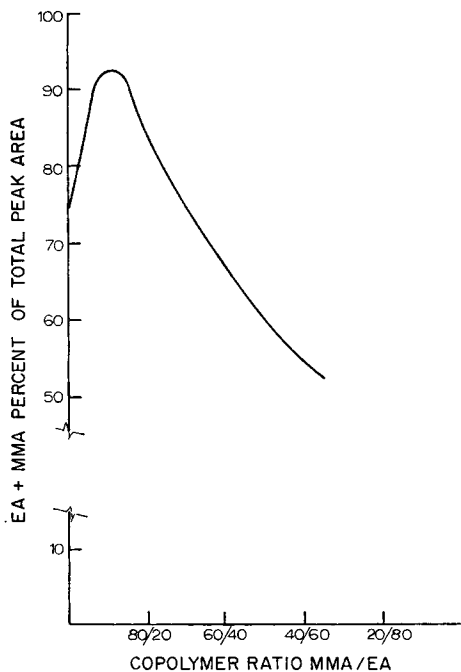


Fig. 2. Fraction of ethyl acrylate and methyl methacrylate in pyrolysis products vs. copolymer composition.

The resulting copolymer, which is assumed to be a random copolymer, is structurally more analogous to a block copolymer. The number of EA-MMA bonds tend to remain constant once the limiting number of EA-MMA bonds have been formed, and they, rather than the size of the ethyl acrylate blocks, determine the amount of ethyl acrylate monomer produced upon pyrolysis. The quantity of each of the major pyrolysis products, ethyl acrylate and methyl methacrylate, can thus be represented by the following expressions:

$$[\text{A monomer}] \propto \text{A-B bonds}$$

$$[\text{B monomer}] \propto \text{B-B bonds}$$

where A is ethyl acrylate and B is methyl methacrylate.

### Sequence Distribution Calculations

To test the above stated hypothesis, sequence distribution calculations were made via a computer with the program of Harwood, Johnston, and Piotrowski,<sup>11</sup> and the number of A-B bonds was determined. It would be expected, on the basis of the pyrolysis work reported, that the relative percentage of A-B bonds remains constant in copolymers of different ethyl acrylate and methyl methacrylate ratios (above 24% ethyl acrylate). The data obtained are shown in Table I.

The sequence distribution data for diad distributions AB + BA (Table I) show some degree of correlation with the prediction for low-conversion copolymers that the relative number of A-B bonds remain constant in copolymers containing different ratios of methyl methacrylate and ethyl acrylate (above 24% ethyl acrylate).

It can be seen that there is a leveling off of the fraction of AB + BA bonds present as the ethyl acrylate content approaches 40%. Correlations with triad, tetrad, and pentad distributions were not observable. Likewise, there were no correlations observed with the number of A sequences or B sequences (calculations included A and B sequences 1 through 10). This is in agreement with the postulation that the size of blocks which occur in the copolymer does not directly affect the amount of ethyl acrylate monomer detected in the pyrolysis products.

High-conversion EA-MMA copolymers of 96% to 100% weight conversion show some discrepancy with the observed correlation for low-conversion copolymers in which the fraction of A-B bonds remains the same as the copolymer composition is varied. However, the direction of changes in the ethyl acrylate peak area agrees with the sequence distribution data, which show that the 60/40 and 40/60 EA-MMA copolymers reach a leveling value for the AB + BA fraction and the 80/20 and 20/80 EA-MMA copolymers exhibit a lower value for the AB + BA fraction. It must be noted that an 80/20 EA-MMA copolymer composition was not achieved in the synthesis of the set of low-conversion copolymers.

In addition, sequence distribution determinations were attempted with nuclear magnetic resonance measurements. Although the chemical com-



positions of the copolymers were determined by integration of the NMR spectra, no information concerning the distribution of monomer sequences has yet been obtainable. This lack of information results from a fundamental difficulty in studying these copolymers. Harwood and Ritchey<sup>12</sup> developed equations for relating the information from NMR to the lengths of sequences or runs. The relations are dependent upon the fact that a given monomer unit A can be in the center of three types of triads: AAA, BAB, and AAB or BAA. Further, the chemical environment of the central A should be different for each of the triads. The difficulty in assessing sequence distributions of the copolymers studied arises because of the similarity between the two monomers employed. A neighboring A unit may not be distinguishable from a neighboring B unit whether the central unit be A or B. A second difficulty arises from stereoregularity considerations. The alpha carbon atom can be the center of either a *d* or an *l* configuration. The observed positions of resonance may not be correlated unambiguously with either the chemical environment or the tacticity.

The sample-handling techniques and sequence distribution calculations discussed herein can be applied to the investigation of pyrolysis products of other copolymer systems. It has been demonstrated that the characterization of poly(methyl methacrylate *co* ethyl acrylate) with pyrolysis gas chromatography is not a simple extension of pyrolysis data obtained with mixtures of homopolymers. In addition, it has been demonstrated that data obtained with pyrolysis gas chromatography applied to copolymer systems can be correlated with sequence distribution calculations and may provide a method for determining the sequence distribution of copolymer materials.

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### References

1. J. Haslam and A. R. Jeffs, *J. Appl. Chem.*, **7**, 24 (1957).
2. E. A. Radell and H. C. Strutz, *Anal. Chem.*, **31**, 1890 (1959).
3. F. A. Lehmann and G. M. Brauer, *Anal. Chem.*, **33**, 673 (1961).
4. R. S. Lehrle and J. C. Robb, *J. Gas Chromatogr.*, **5**, 89 (1967).
5. L. A. Wall and R. E. Florin, *J. Res. Nat. Bur. Stand.*, **60**, 451 (1958).
6. C. G. Esposito, *Anal. Chem.*, **36**, 2183 (1964).
7. J. Strassburger, G. M. Brauer, M. Tryon, and A. F. Forziati, *Anal. Chem.*, **32**, 454 (1960).
8. R. L. Levy, *J. Gas Chromatogr.*, **5**, 107 (1967).
9. F. Farré-Rius and G. Guiochon, *Anal. Chem.*, **40**, 998 (1968).
10. M. L. Yeagle and R. W. Scott, Proceedings of the Meeting of the ACS Division of Organic Coatings and Plastics Chemistry, Atlantic City, September 1968, p. 51.
11. J. H. Harwood, N. W. Johnston, and H. Piotrowski, *Amer. Chem. Soc. Polymer Reprints*, **8**, 199 (1967).
12. J. H. Harwood and W. M. Ritchey, *J. Polym. Sci. B*, **2**, 601 (1964).

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