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Progress Report

ANALYSIS OF METHYL METHACRYLATE COPOLYMERS BY GAS CHROMATOGRAPHY

by

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Abstract

The usefulness of gas chromatographic techniques for the identification of selected polymers and the quantitative determination of the composition of copolymers was investigated.

In the procedure employed the polymer or copolymer was characterized from the chromatogram of its liquid pyrolysis products. Presence of copolymeric constituents even in amounts of 1% or less was readily detected. A rapid method of improved accuracy for the quantitative determination of methyl methacrylate copolymers has been developed.

1. INTRODUCTION

The detection and quantitative determination of copolymeric constituents in polymers such as methyl methacrylate is a difficult and tedious task. Especially difficult to analyze are the compositions of cross-linked insoluble polymers. Often the compositions cannot be determined with any degree of accuracy. Most practical procedures identify the pyrolysis products of the insoluble copolymers by infra-red or mass spectrometric techniques.

Recently gas chromatography has become one of the most useful tools for the separation, identification and quantitative

analysis of volatile organic compounds. In this technique separation of components of a mixture is accomplished by selective sorption on a stationary medium. Although a number of books [1-3] and papers have described gas chromatographic separation of organic mixtures, only a few investigators [4-7] have reported identification of polymers by gas chromatographic analysis of their pyrolysis products.

The aim of this study was to determine the suitability of gas chromatographic techniques for the identification of polymers used in dentistry. The materials were depolymerized and the liquid fractions of the depolymerization products were subjected to vapor chromatographic analysis. Among the materials studied were mixtures and copolymers of methyl methacrylate with methyl and ethyl acrylate, acrylic and methacrylic acid and ethylene dimethacrylate.

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

The copolymers were bulk polymerized after removal of the inhibitor from the monomer either by extraction with sodium hydroxide or by distillation. Solutions containing varying percentages of monomers (by volume) were placed into clean test tubes and nitrogen was bubbled through each sample for five minutes. The test tubes were immediately stoppered with an aluminum foil covered cork and placed in a 60°C oven and were kept at this temperature until the contents had polymerized to a solid mass.

They were then placed in a 100° C oven for two to three days to complete the polymerization. In later experiments the test tubes were sealed in order to avoid loss of volatile monomer due to evaporation during polymerization.

The polymers were pyrolyzed in an oven at 350° C and the liquid fraction of the pyrolysate was collected in a covered container kept in an ice bath. Although precautions were taken to avoid loss of highly volatile liquids, slight errors in the subsequent analysis may have been caused by the evaporation of such components. No effort was made to collect gaseous pyrolysis products and hence they did not appear in the chromatograms. The pyrolysis condensates were stored in snap cap vials in a refrigerator prior to analysis which was usually conducted within 48 hours. Samples were removed from the vials by means of a Gilmont micropipet syringe and 20 microliters were introduced into the injection valve of the chromatograph.

2.2 Apparatus and Operating Procedures

Analyses were made using a Consolidated Electrodynamics Corporation chromatograph, type X-26-201. A schematic drawing is given in Figure 1. A small amount of sample was injected at the head of the partition column and was transported through the column by helium which acted as an inert carrier gas. The column was made up of an inert size-graded solid that functioned as the support for the stationary liquid phase. Johns-Manville C-22 ground firebrick, mesh #30 to 70, was selected as the solid support for dinonyl phthalate, the liquid phase.

Dinonyl phthalate, a liquid with low vapor pressure, was employed as the stationary phase since it is non-selective; that is, it will effect a satisfactory separation for a wide range of compounds, roughly according to their volatility and can be used at relatively high temperatures. The columns were prepared according to the procedure described by Dimbat, Porter and Stross [8].

The temperature of the column was kept high enough to vaporize the sample. Thus, the carrier gas carried the vaporized components of the sample through the column at different rates in accordance with the relative degree of volatility of the components, causing them to emerge from the end of the column in the order corresponding to their affinity for the column material. Changes in the composition of the effluent were detected by a delicate sensing device, capable of indicating both qualitatively and quantitatively the presence of components in the effluent. This detector consisted of four thermal conductivity cells arranged in the form of a Wheatstone Bridge. At the start of the experiment when pure carrier gas was passed through all four cells the bridge was balanced. When column effluent passed through two of the cells, the difference in thermal conductivity of the pure carrier plus material eluted from the column caused an unbalance in the bridge. The signal resulting from the unbalance was amplified and the presence of a vapor in the effluent helium gas was recorded as a peak. The time at which the peak occurred

(retention time) was characteristic for each compound and served for its detection and identification. Areas under the peaks or the ratio of peak heights were used for the quantitative determination of the components of a mixture. Details of the operating conditions are given in Table 1.

3. RESULTS

3.1 Qualitative Identification

Identification of various copolymers containing 50%, 90% and 99% methyl methacrylate were made by chromatographic analysis of their pyrolysis products. All components of these pyrolysis products were detected by characteristic peaks at definite retention times which were reproducible within ± 5 seconds. Figures 2-4 show typical chromatograms of copolymers. Similar monomeric components of the copolymers such as methyl and ethyl acrylate (Figure 2 Top and Figure 2 Bottom) or acrylic and methacrylic acid (Figure 3 Top and Figure 3 Bottom) give peaks at approximately the same retention times. However, the pyrolysis products of these copolymers are in different proportions as evidenced by the variations in the areas under the peaks as well as the peak heights.

Small amounts of copolymeric components can be readily detected. The presence of 1% copolymer in poly(methyl methacrylate) always produced a distinct additional peak besides the single major peak due to methyl methacrylate. Even 0.2% of copolymeric constituents could be detected but their qualitative identification from the chromatograms was not readily possible. With modification of the

sensing device it should be possible to increase considerably the sensitivity of detection of copolymeric constituents.

Poly(methyl methacrylate) degrades with the formation of its monomer as the only depolymerization product. Even when other copolymeric constituents are present poly (methyl methacrylate) on heating reverts to its monomer. Hence, the chromatograms of all methyl methacrylate copolymers will have one peak due to this component and a number of other peaks which are caused by the other constituents. Methyl methacrylate always gave the most prominent peak in the chromatograms and in the accompanying figures its peak height has been scaled down by a factor of 10 in order to show the other peaks more distinctly. Although it was not the main object of this study to identify pyrolysis products, the identity of some of the peaks was established by comparison with known compounds suspected to be present. Furthermore, for methyl acrylate polymer the peaks were partially identified from the mass spectrographic analysis of the pyrolysis products reported by Straus and Madorsky [9].

Variations in the amounts of monomeric constituents in the copolymer were readily distinguished by changes in the peak heights on the chromatogram.

3.1.1 Differentiation of Polymer Mixtures and Copolymers

The chromatographic technique was employed to distinguish polymer mixtures and copolymers. Pyrolysis products of polymers containing one recurring monomer unit were mixed in definite

proportions. As can be seen from Figure 5, chromatograms of the pyrolysis products of polymer mixtures and of copolymers containing the same ratio of monomeric constituents are not identical. Although similar degradation products are formed, their quantities as determined by peak heights are different. For instance, the amount of methanol in the mechanical mixture of the pyrolysis products of methyl methacrylate and methyl acrylate polymers is much larger than in the pyrolysis condensate of the copolymer of the same composition. Hence, due to the different amounts of degradation products formed it is possible to distinguish between homogeneous copolymers and mechanical polymer mixtures of the same composition.

3.2 Quantitative Determination

3.2.1 Mechanical Mixtures

A series of mixtures of pyrolysis products mixed after depolymerization were used as standards to evaluate the precision of the method and also to study the reproducibility of the instrument. The per cent composition of the pyrolysis products varied from 50% to 90% methyl methacrylate. Each sample was analyzed at least three times. Due to the lack of sufficient thermal conductivity data for the components of the pyrolysis mixtures it is difficult to accurately determine the absolute quantities of the compounds present from the areas under the peak. However, in all chromatograms a few sharp, characteristic, symmetrical peaks of reproducible height are present. Two or more representative peaks

that are attributable to two components of the mixture are chosen for the calculation of the peak height ratios. From the ratios of a series of standard mixtures of known polymeric composition, a calibration curve, which serves for the determination of the composition of an unknown polymer mixture, is obtained. The relative areas under the peaks have also been used for calculating the polymeric composition. Since the curves selected from the chromatograms are quite similar in base width and shape, use of the peak height ratios is simpler and gives results of the same order of precision as those arrived at from measuring the areas under the peak by means of a planimeter.

Figure 6 shows a plot of the average peak-height ratio versus per cent composition for methyl methacrylate - methyl acrylate polymer mixtures. Since the two main pyrolysis products of poly(methyl acrylate) are methanol and methyl acrylate and that of poly(methyl methacrylate) is its monomer, the ratio of the peak height of

$$\frac{\text{methanol + methyl acrylate}}{\text{methyl methacrylate}}$$

is used. Duplicate chromatographic analyses of the pyrolysis mixture show little variation in the peak-height ratios. The standard deviations of these ratios lie within the diameters of the circles surrounding the average values. From this curve the per cent composition of an unknown polymer mixture can be determined to better than ±0.5%.

Substituting for the peak-height ratio, $\left(\frac{\text{methanol + methyl acrylate}}{\text{methyl methacrylate}}\right)$, the ratios of the peak height, $\frac{\text{methanol}}{\text{methyl methacrylate}}$ or $\frac{\text{methyl acrylate}}{\text{methyl methacrylate}}$, does not appreciably change the precision of the results.

3.2.2 Copolymers

From the chromatogram of the pyrolysis products of a copolymer a quantitative analysis of the copolymeric components can be made. Two copolymeric systems, that of methyl methacrylate -methyl acrylate and methyl methacrylate-ethylene dimethacrylate, were studied. Two specimens were made for the first copolymer system (MMA-MA), and four specimens for the second system (MMA-EDMA), for each composition. Figures 7 and 8 show graphs of peak height ratios versus composition for these two copolymer systems. Average values and standard deviations are indicated at each composition. The curves are fitted to the average values and the vertical bars represent ± two standard deviations. These deviations represent the precision for a single analysis of a copolymer sample of unknown composition.

From the standard curves the composition of the copolymer can be determined with a precision of ± 2 or 3% in the upper portion of the curve and within ± 1.0% when the percentage of poly (methyl methacrylate) is less than 20%. A polymer prepared from a commercial monomer solution containing 81% methyl methacrylate and 19% ethylene dimethacrylate was analyzed using this standard analysis curve. The results were well within 1% of its true composition.

The precision of the analysis was always better with materials containing high percentages of methyl methacrylate. This greater precision did not result from instrumental errors or even from preparation of the polymer since polymerization of the material in sealed test tubes did not bring about a reduction in the standard deviation. Undoubtedly, therefore, the greatest inaccuracy was due to the method of depolymerization or the mechanism therein, despite the fact that precautions were taken to conduct this procedure under identical conditions. Copolymers containing about equal amounts of methyl methacrylate and a second component are more likely to be influenced by slight changes in the operating procedure of the depolymerization than are polymers high in methyl methacrylate since the degradation mechanism of the former is more complex and results in the formation of a larger number of very volatile products. The loss of some volatile constituents such as methanol or methyl or ethyl acrylate may occur even though the receiver in which the pyrolysis products are collected is cooled in an ice bath. Furthermore, chromatographic analysis of the pyrolysis products was usually carried out within 24 to 48 hours after degradation. During this time some change in the multicomponent reaction mixture may take place. As a matter of fact marked changes in the composition, as evidenced by variations of the chromatograms, were observed after storage of the pyrolysis liquids for a few months.

In order to alleviate the shortcomings of this pyrolysis technique the chromatographic inlet system has been modified so

that the decomposition products of a polymer sample pyrolyzed by means of a hot wire are carried directly into the column. Results obtained using this redesigned sample inlet system will be described in a future report.

SUMMARY

Copolymers of methyl methacrylate were depolymerized and the liquid pyrolysis products were analyzed by gas chromatography. Presence of copolymeric constituents in the polymers could be detected by the presence of additional peaks. Quantitative determination of the composition of methyl methacrylate copolymers could usually be accomplished within 2%. Ease of analysis, speed, and an improved accuracy make this chromatographic technique suitable for the qualitative and quantitative determination of methyl methacrylate copolymers.

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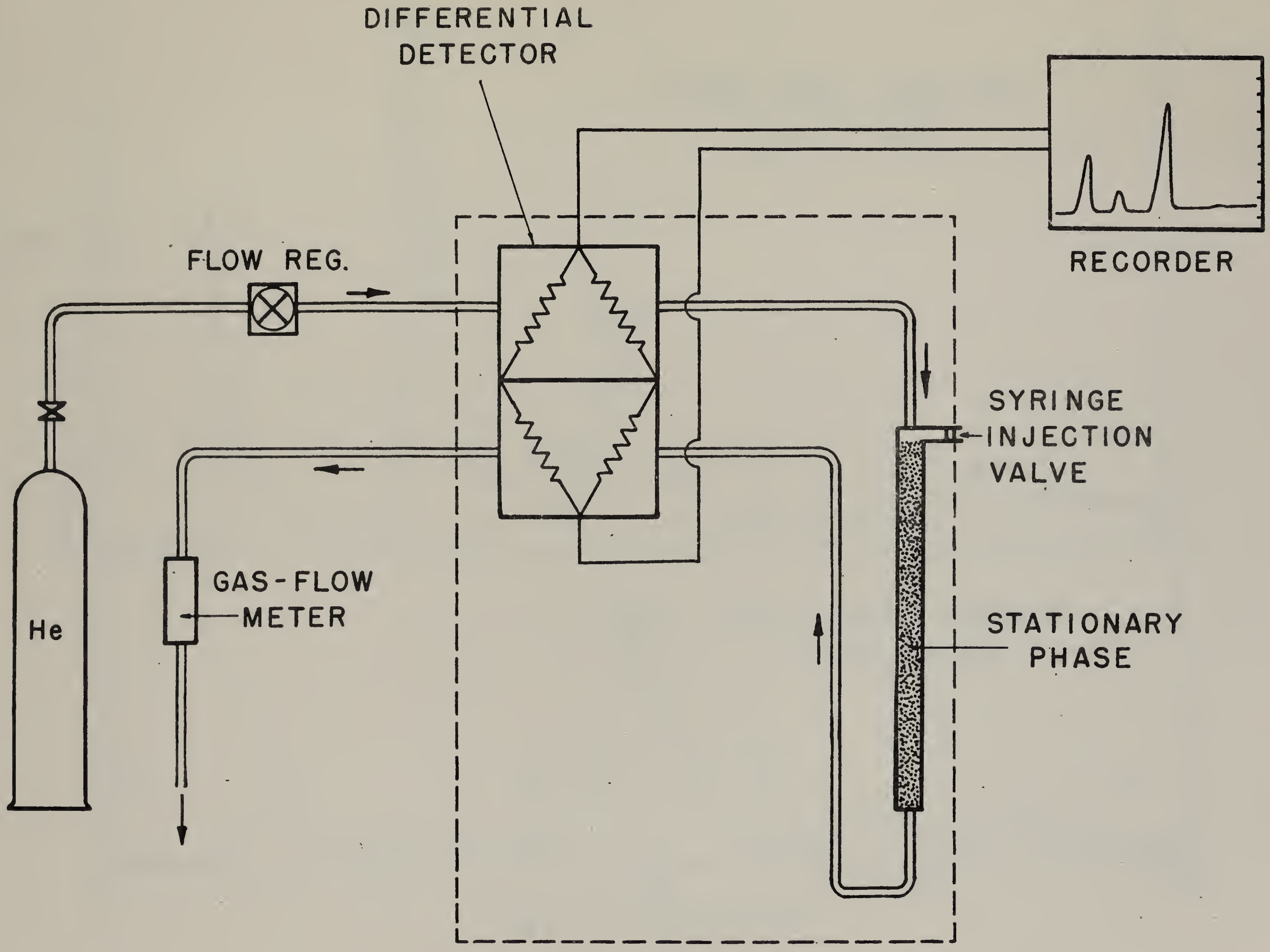
TABLE 1

OPERATIONAL CONDITIONS

1. Column length - 6 ft.
2. Bore - 3/16 in. diam.
3. Column material - dinonyl phthalate on ground fire brick
4. Carrier gas - helium
5. Flow rate - 50 ml/min
6. Pressure head - 20 psi
7. Column temperature - 150° C
8. Sample quantity - 20 μl



SCHEME OF CHROMATOGRAPH

FIGURE 1.

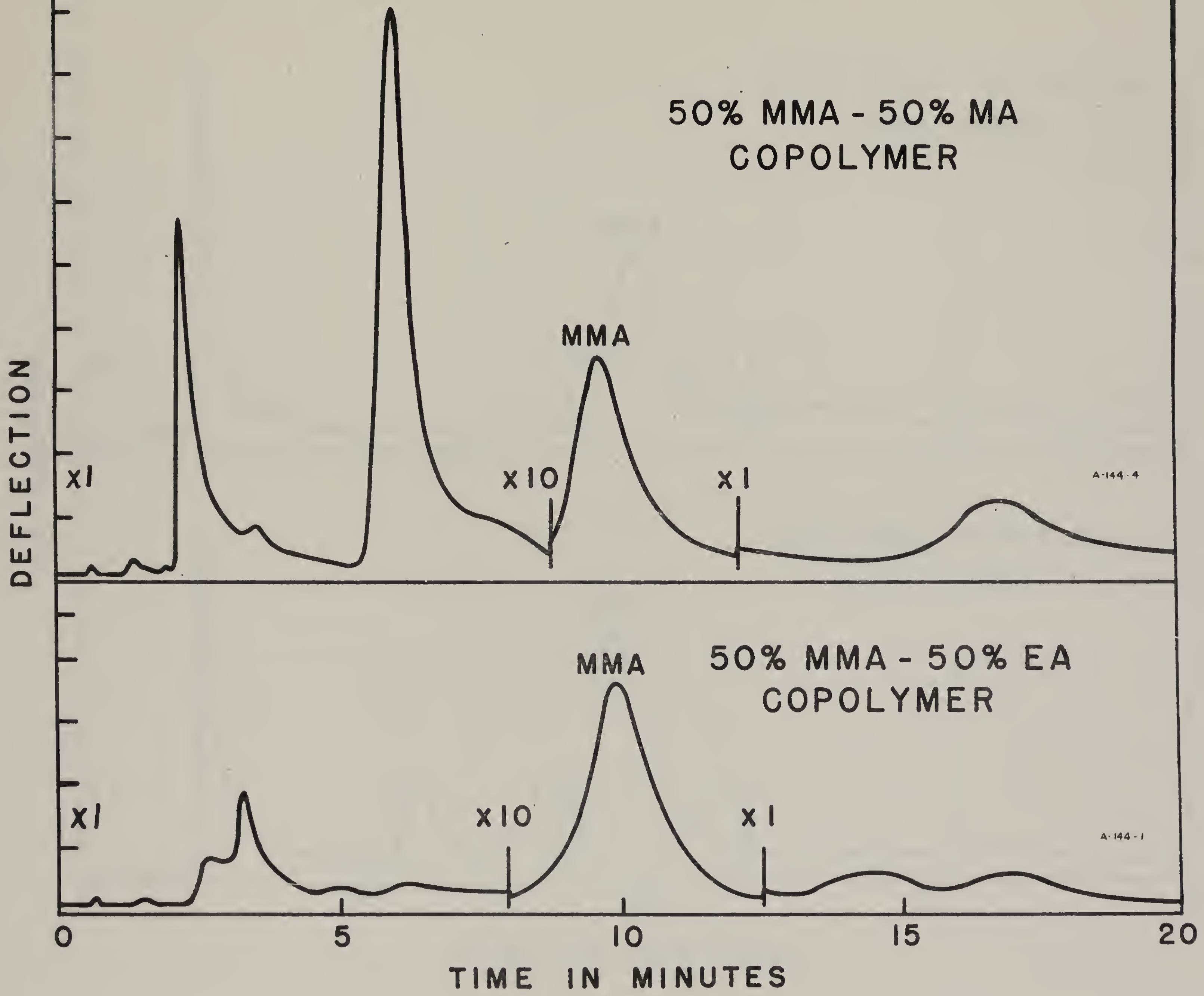


Figure 2. Typical chromatograms of pyrolysis products.

TOP : 50% methyl methacrylate (MMA).
50% methyl acrylate (MA) copolymer.
BOTTOM: 50% methyl methacrylate (MMA).
50% ethyl acrylate (EA) copolymer.

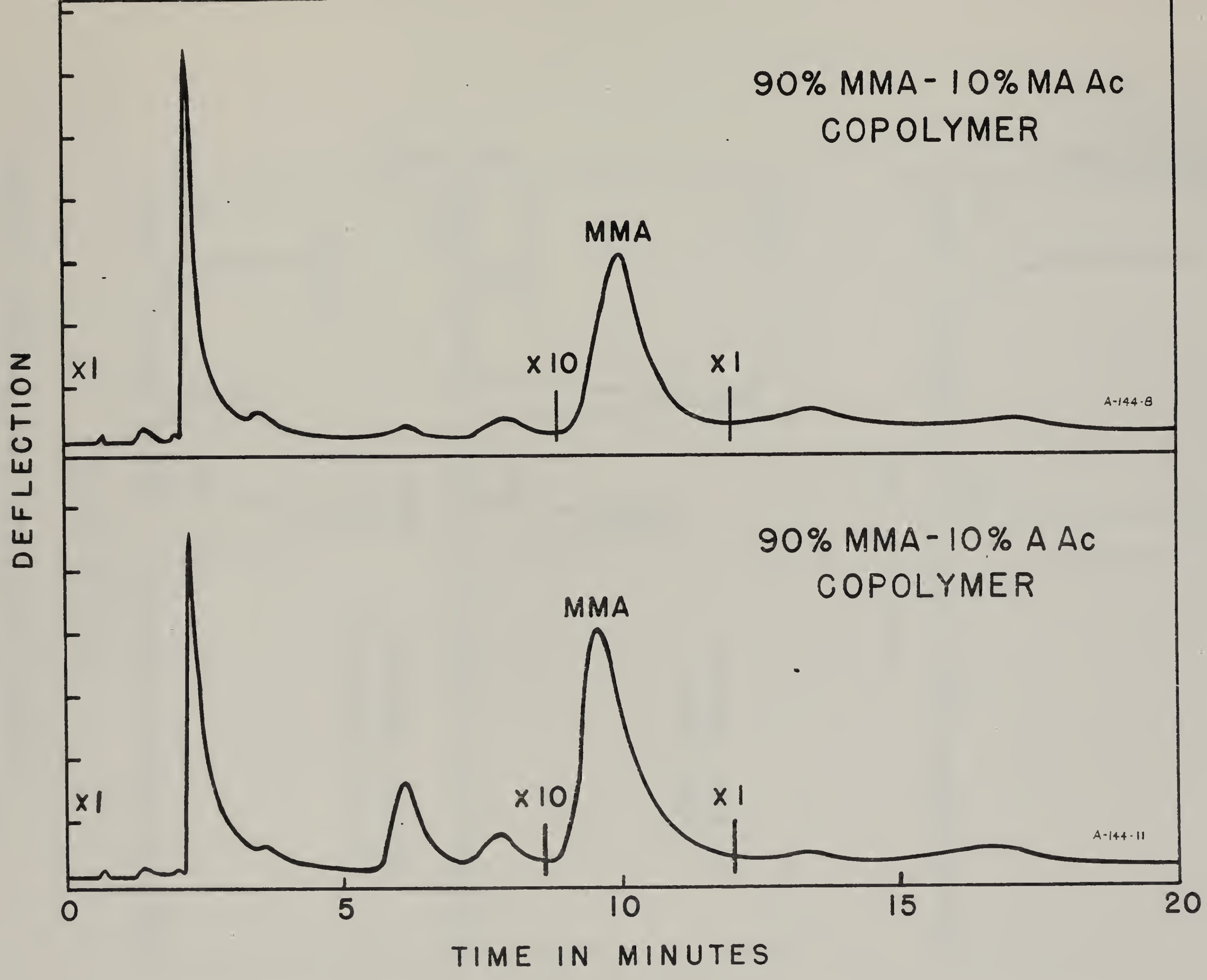
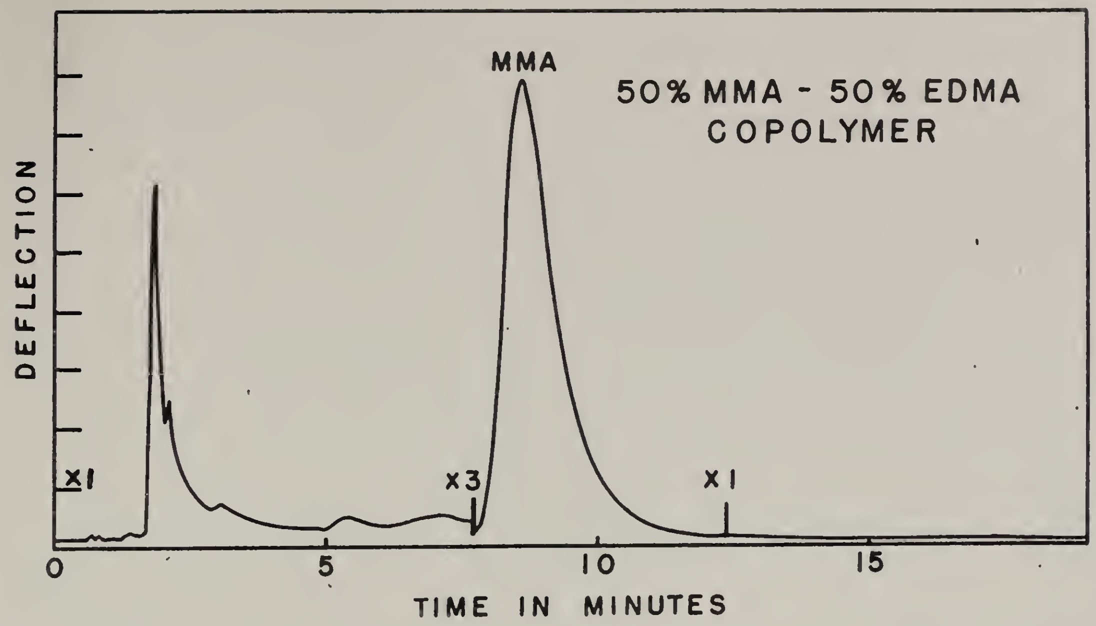
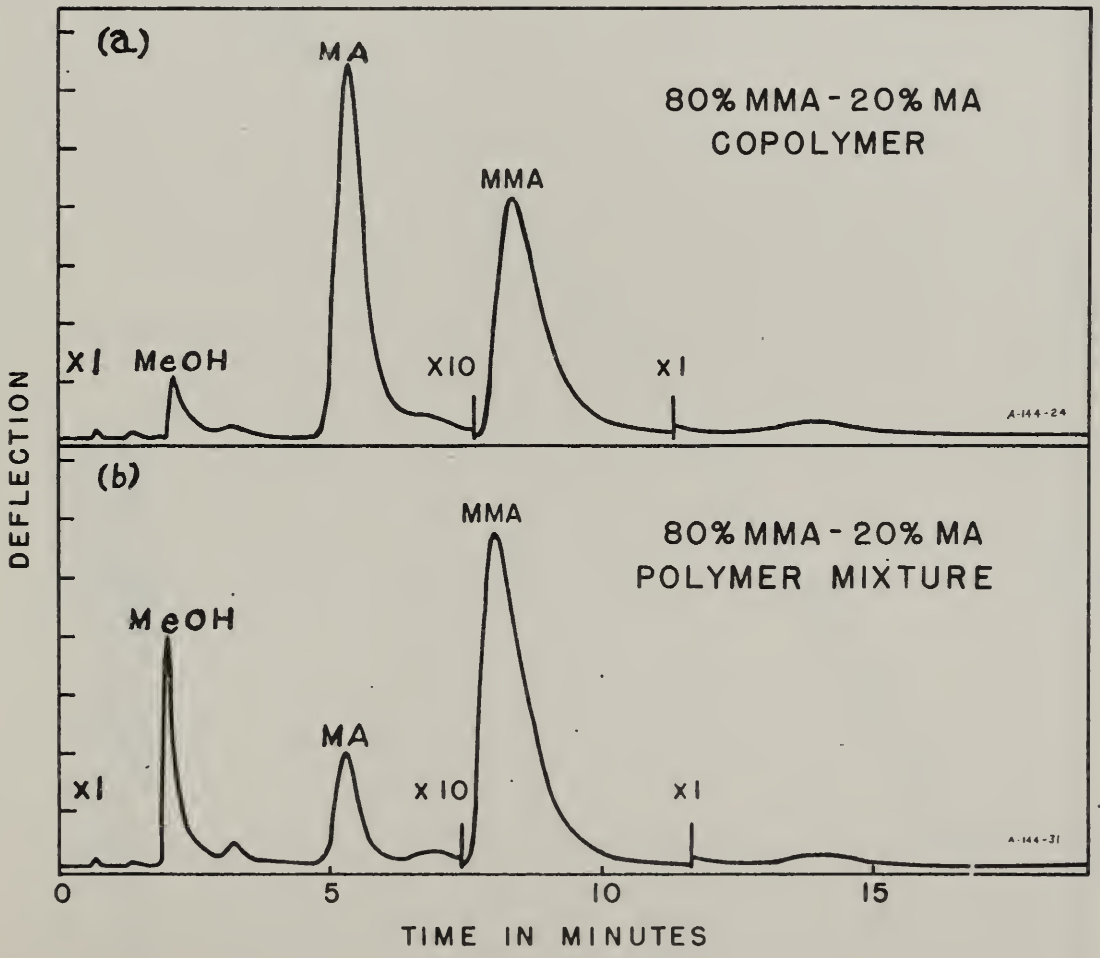


Figure 3. Typical chromatograms of pyrolysis products.

TOP : 90% methyl methacrylate (MMA).
10% methacrylic acid (MAAc) copolymer.
BOTTOM: 90% methyl methacrylate.
10% acrylic acid (AAc) copolymer.





Typical chromatograms of pyrolysis products.

TOP : Figure 4. 50% methyl methacrylate (MMA).
50% ethylene dimethacrylate (EDMA) copolymer.

BOTTOM: Figure 5. 80% methyl methacrylate (MMA)
20% methyl acrylate (MA).

a. Copolymer.
b. Polymer mixture.

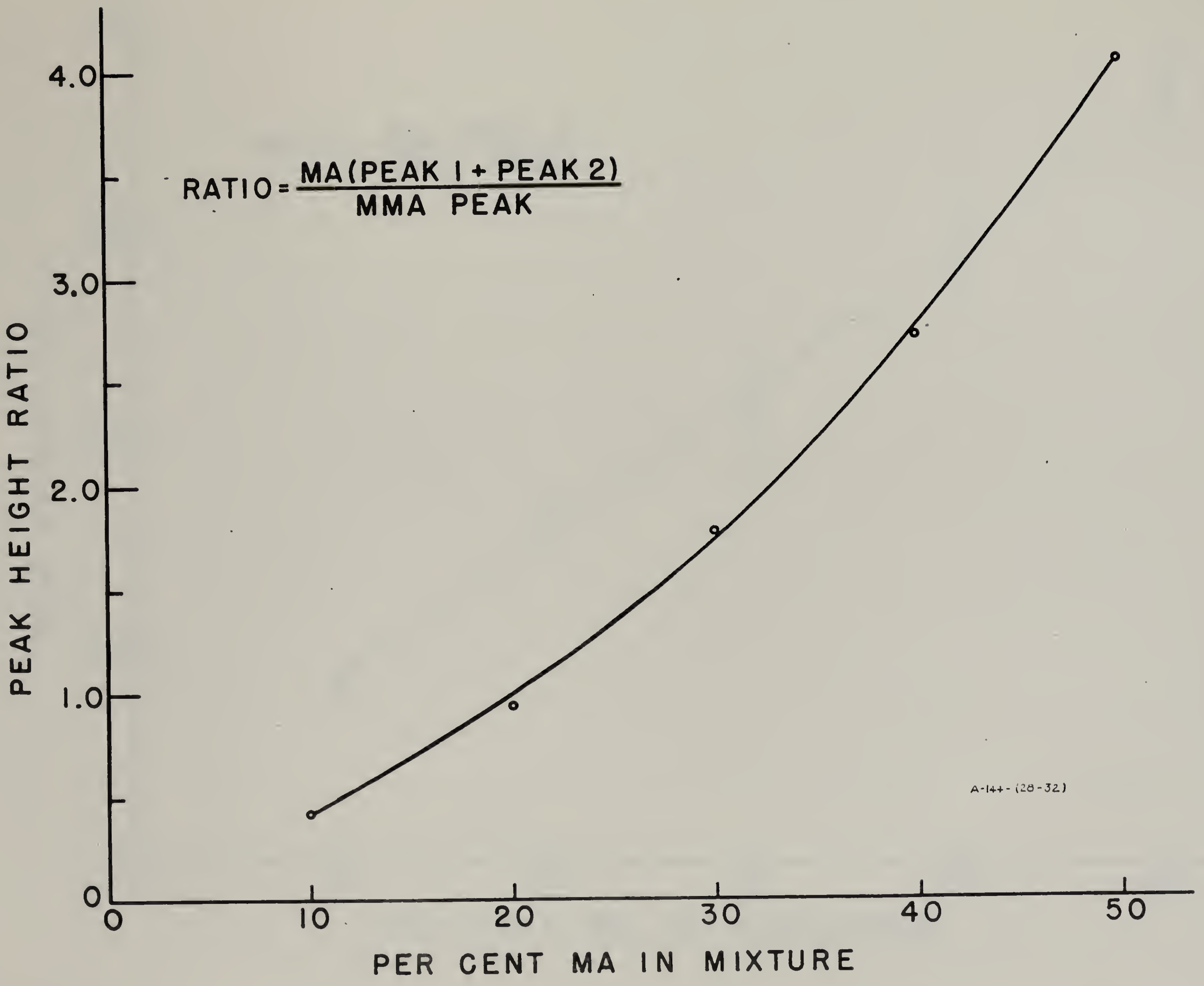


Figure 6. Analysis curve of a series of mixtures of methyl methacrylate (MMA) - methyl acrylate (MA) pyrolysis products.

Peak 1 = MeOH peak.
Peak 2 = MA monomer peak.

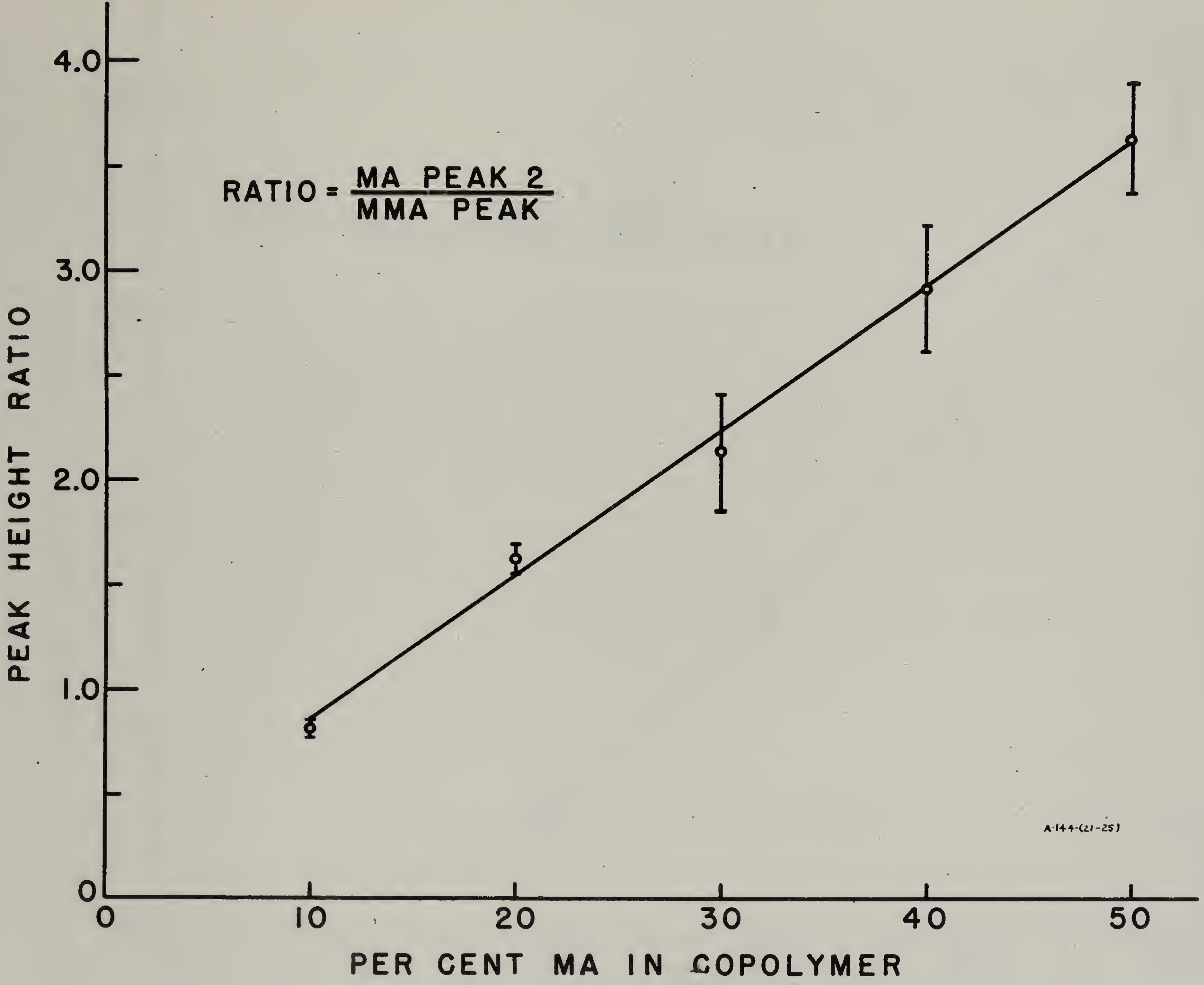


Figure 7. Analysis curve of a series of methyl methacrylate (MMA) - methyl acrylate (MA) copolymers.

MA Peak 2 = MA monomer Peak.

[illegible]

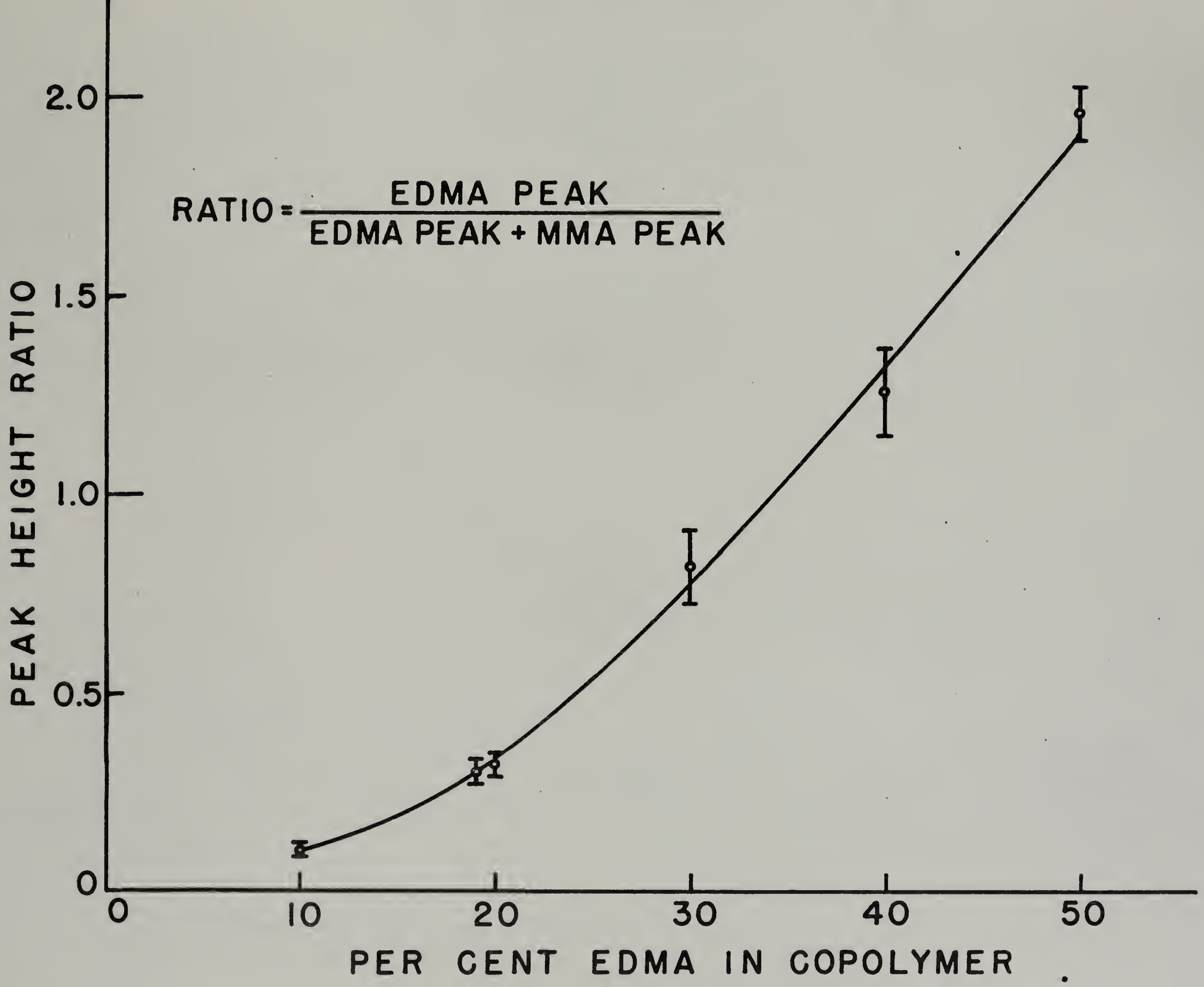


Figure 8. Analysis curve of a series of methyl methacrylate (MMA) - ethylene dimethacrylate (EDMA) copolymers.