

## Analysis of Polymethacrylates by Gas Chromatography

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### INTRODUCTION

In the course of a program on the synthesis of methacrylate polymers, it was found desirable to have a rapid, quantitative test to determine the composition of copolymers of various esters of methacrylic acid. Such an analysis presented difficulties because of the many different esters available which differ only slightly in their chemical and physical properties. In some cases, hydrolytic methods can be used to determine the ester constituents of the polymer. For example, Haslam, Hamilton, and Jeffs<sup>1</sup> determined ethyl acrylate in methyl methacrylate copolymers by converting the alkoxy groups in the sample to the corresponding iodides, which were then determined by gas chromatographic methods. Thermal decomposition of the polymer followed by analytical distillation is a possible method, but it is time-consuming and requires relatively large amounts of material.

Since it was known that such copolymers, when heated above a certain "threshold" temperature, will depolymerize to give nearly quantitative yields of the corresponding monomers, it appeared that a feasible method would be to thermally degrade the copolymers to monomers and then analyze the products by gas chromatography. A further refinement which made the method much more attractive was the possibility of degrading the polymer in the entrance to the gas chromatographic column with a hot wire.

This approach was tried with a number of copolymers of methacrylic esters and was found to be reliable and rapid. The results appear to be good enough for quantitative determinations if suitable standards can be prepared for calibration of the apparatus.

### APPARATUS

Two Pyrex glass columns, 120 cm. long and 0.54 cm. in i.d., with a T-section at one end for injecting the sample were used. Each column was con-

nected to one side of a thermal conductivity cell. The cell and the columns were insulated and heated with resistance wire. Each column was packed with 6.5 g. of 30% Apiezon K supported on Celite 545 (60-115 mesh).

Two temperatures were necessary to analyze the range of esters of interest. A column at 160°C. was used to separate the low molecular weight esters from C<sub>2</sub> to C<sub>10</sub> alcohols, and a column at 255°C. was satisfactory for the esters from C<sub>8</sub> to C<sub>18</sub> alcohols. If methyl methacrylate is of interest, a temperature lower than 160°C. is necessary, since at this temperature the methyl methacrylate peak is almost superimposed on the air peak.

The sample holder was made from 1 in. of Nichrome wire (B. and S. No. 32, 10.9 ohms/ft.) spiraled in a compact coil with each end passed through a silicone rubber seal (Burrell seal No. 261-8).

A Gow-Mac thermal conductivity cell model 9193 (TE-11) was used as the detector.

A Speedomax (Leeds and Northrup Co.) recorder with a 6-mv. range was used.

A Leeds and Northrup microvolt amplifier was used with some samples for improving the sensitivity of analysis for trace compounds.

Two flowmeters with capillary orifices and silicone oil manometers were used to measure the flow rate of the carrier gas.

### PROCEDURE

The conditions used for the analyses with the gas chromatographic apparatus were as follows:

Helium flow rate	= 75 ml./min.
Temperature, column 1	= 160 ± 2°C.
Temperature, column 2	= 255 ± 2°C.
Inlet pressure, column 1	= 2.0 psig
Inlet pressure, column 2	= 2.8 psig
Outlet pressure	= 14.7 psia
Temperature of detector	= 285 ± 2°C.
Current on bridge	= 130 ma.
Sample size	= 10 to 50 mg.

The sample to be analyzed was dissolved in acetone or benzene (1 to 10% concentration). The wire coil of the sample holder was dipped into this solution and allowed to dry a few minutes in a circulating-air oven at 50°C. (One coating is usually sufficient, but several layers can be applied if needed. It is important that a thin, homogeneous film be formed on the wire. The correct solution concentration and film thickness are found by a few trials.) The prepared sample holder was then placed in the gas stream of the chromatographic apparatus in place of the injection cap. After equilibrium was obtained, a voltage sufficient to heat the wire to a dull, red heat was applied for 15 sec. This voltage was generally in the range of 5–15 v. (The heating causes little disturbance in the base line. If the voltage is too high, extraneous peaks will appear in the chromatogram, presumably because of thermal decomposition of the monomer.) The end of the heating period was taken as the zero time for measurement of the elution time of each constituent.

The constituents were identified by their elution times or by their specific retention volumes  $V_g^\circ$ . The area under each elution peak as measured by a compensating polar planimeter (K and E 4236 M) was taken as an estimate of the weight percentage of that constituent present. (The completeness of the degradation may be tested by reapplying current to the wire. If no further peaks are obtained, the polymer is assumed to be completely degraded.)

## RESULTS AND DISCUSSION

The specific retention volumes of some methacrylates are given in Table I. The compounds eluted were identified by using, if possible, the pure ester. In a few cases, the eluted compound was identified as a known impurity in a commercial methacrylic ester. The compounds thus identified were octyl, myristyl, and cetyl methacrylates.

The specific retention volume  $V_g^\circ$  is the volume of gas per gram of stationary phase required to elute each constituent from the chromatographic column. It is calculated by the following formula:<sup>2</sup>

$$V_g^\circ = 273 F_m f(t_x - t_0) / T_m W$$

where  $T_m$  is the absolute temperature of the flowmeter (298°K.),  $W$  is the weight of stationary phase in column packing (1.95 g.),  $F_m$  is the flow of carrier gas (in milliliters per minute) at temperature

TABLE I  
Specific Retention Volume of Methacrylic Esters

Compound	No. carbon atoms in alcohol part	Specific retention volume, ml./g.	
		160°C.	255°C.
Ethyl methacrylate	2	15.8	1.6
Butyl methacrylate	4	33.5	3.2
2-Diethylaminoethyl methacrylate	—	47.5	—
Hexyl methacrylate	6	89.7	6.5
2-Ethyl-4-methylpentyl methacrylate	8	142.7	—
Octyl methacrylate	8	213.0	14.5
Decyl methacrylate	10	603.0	24.2
Lauryl methacrylate	12	—	50.1
Myristyl methacrylate	14	—	92.1
Cetyl methacrylate	16	—	188.0
Stearyl methacrylate	18	—	344.0

of flowmeter, and  $f$ , a reducing factor for pressure drop across column is given by

$$f = \frac{3}{2} [(P_i/P_o)^2 - 1] / [(P_i/P_o)^3 - 1]$$

$P_i$  and  $P_o$  being the inlet and outlet pressures, respectively, and  $t_x$  and  $t_0$  are the times for emergence of sample  $x$  measured at peak maximum, and

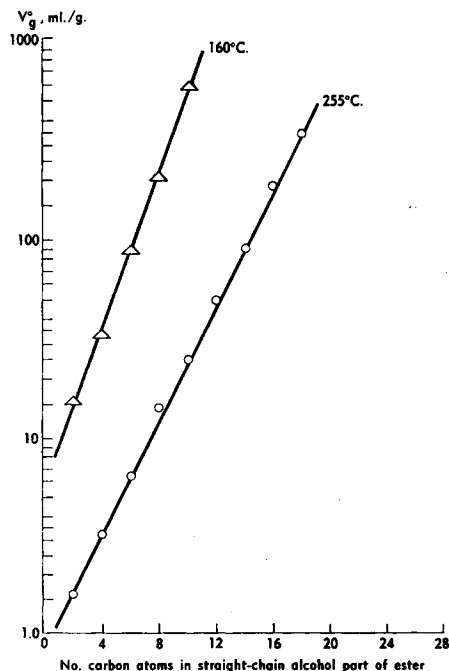


Fig. 1. Specific retention volume of methacrylates as a function of the number of carbon atoms in the alcohol.

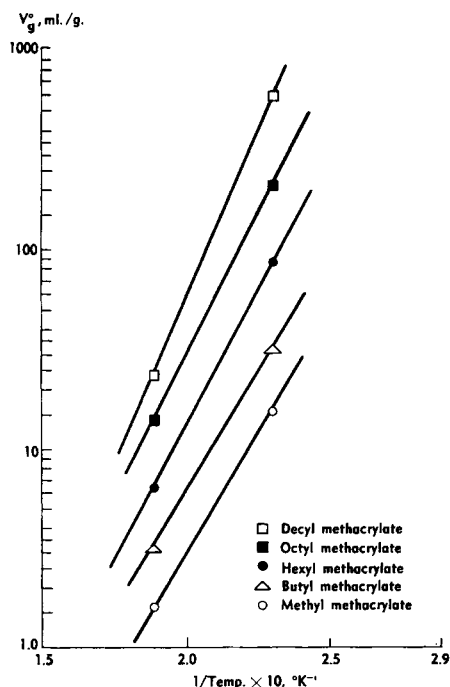


Fig. 2. Variation of specific retention volume with temperature.

air measured at peak maximum (0.15 min.), respectively.

The column resolution was not very great for these esters, being only about 590 theoretical plates for the higher boiling esters.

It was found that a plot of the logarithm of the specific retention volume against the number of carbon atoms in the alcohol part of the ester yielded a straight line from which values could be predicted for any unknown member of the series. Plots of the values obtained at 160 and 255°C. are shown in Figure 1.

It should be pointed out that this relation holds only for the straight-chain esters. The values of  $V_g^0$  for branched-chain esters, such as 2-ethyl-4-methylpentyl methacrylate, fall below the lines shown in Figure 1.

From theoretical considerations,<sup>3</sup> it is expected that a family of parallel straight lines should be obtained when the logarithm of the specific retention volume is plotted against the reciprocal absolute temperature  $1/T$  for a homologous series of chemical compounds. Such plots are shown in Figure 2 for esters of  $C_2$  to  $C_{10}$  straight-chain alcohols. It is seen that, assuming the straight-line relation, the lines are approximately parallel except for that for the  $C_{10}$  ester. The average activation energy for the specific retention volume of these esters is

-12.4 kcal. With the use of this relation, the value of the specific retention volume at any temperature can be predicted once the value has been determined at one temperature. The value of the specific retention volume at temperature  $T_1$  is related to the value at temperature  $T_2$  ( $^{\circ}K.$ ) by the equation:

$$\log (V_g^0)_{T_1} = \log (V_g^0)_{T_2} + (\partial \log V_g^0) / \partial (1/T) [(1/T_1) - (1/T_2)]$$

For unknown methacrylates, the value of  $(V_g^0)_{T_2}$  can be obtained by interpolation or extrapolation of the curves shown in Figure 2.

The results obtained by use of the hot-wire technique to analyze some copolymers of butyl methacrylate and hexyl methacrylate are given in Table II. These copolymers were prepared by bulk polymerization in presence of lauroyl peroxide as a catalyst at 80°C., dissolved in acetone, and analyzed. The peaks due to air and acetone trapped in the polymer film were eliminated from the calculations. There was also an impurity (about 5%) in the hexyl methacrylate monomer which also appeared in the analysis. This impurity was probably isohexyl methacrylate and was included in the analysis as hexyl methacrylate. The butyl methacrylate content of these copolymers was found by analysis to be 2-3% higher than the content of the monomer mixtures. Since this is just outside of the experimental error, it must be assumed that the butyl methacrylate has a greater reactivity in the copolymerization than the hexyl methacrylate.

It appears that this method of analysis can be applied, at least qualitatively, to the analysis of any polymer which can be thermally degraded to give characteristic products. For example, polystyrene gives the characteristic peak due to styrene monomer, and polyethylene and polypropylene give peaks corresponding to the series of hydrocarbon residues formed during the thermal degradation. If the conditions are closely reproduced, it is possible to identify any polymer by the characteristic spectrum of peaks formed by thermal cracking on the hot wire. When thermal decomposition yields monomer exclusively, the method is not only qualitative but quantitative (see Table II). Polymers which decompose in this way are generally those which contain an alpha alkyl substituent.<sup>4</sup> However, it is possible that even with copolymers which do not decompose exclusively to give monomers, the method can be made quantitative by careful calibration with known samples.

TABLE II  
Analyses of Homopolymers and Copolymers of Butyl Methacrylate and Hexyl  
Methacrylate by Gas Chromatography

	Sample				
	A	B	C	D	E
Wt. ratio, butyl/hexyl methacrylate in copolymer	100.0/0.0	75.3/24.7	51.1/48.9	23.7/76.3	0.0/100.0
Conversion to polymer, %	95.6	96.5	94.6	94.9	94.6
Av. wt. ratio, butyl/hexyl methacrylate in polymer	100.0/0.0	77.6/22.4	54.2/45.8	25.9/74.1	0.0/100.0
No. of analyses	3	6	6	4	3
Standard deviation of analyses for butyl methacrylate in polymer, %		1.4	1.1	2.2	

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### References

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### Synopsis

A rapid and reliable method has been developed for the analysis of polymethacrylates. The polymer was decomposed on a heated wire at the entrance to a gas chromatographic column, and the monomeric constituents were identified from the resulting elution curve. Data on the specific retention volumes on an Apiezon K column are reported for a number of esters of methacrylic acid from straight-chain alcohols ranging from C<sub>2</sub> to C<sub>18</sub>. Methods are described for predicting the retention volumes of unknown methacrylic esters at any temperature. The method shows promise for the analysis of copolymers from a wide range of vinyl monomers.

### Résumé

Une méthode rapide et sûre a été développée pour l'analyse des polyméthacrylates. Le polymère est décomposé sur un fil métallique chauffé à l'entrée d'une colonne de chromatographie gazeuse, et les constituants monomériques sont identifiés à partir de la courbe d'éluion. Des résultats sur les volumes de rétention spécifiques sur une colonne Apiezon K sont indiqués pour un nombre d'esters d'acide méthacrylique à partir des alcools à chaîne normale allant de C<sub>2</sub> à C<sub>18</sub>. On décrit des méthodes pour prédire les volumes de rétention d'esters méthacryliques inconnus à chaque température. La méthode semble prometteuse pour l'analyse d'un grand nombre de copolymères avec des monomères vinyliques.

### Zusammenfassung

Eine rasche und verlässliche Methode zur Analyse von Polymethacrylaten wurde entwickelt. Das Polymere wurde an einem erhitzten Draht an der Öffnung einer Gaschromatographiesäule zersetzt und die monomeren Bausteine wurden aus der resultierenden Elutionskurve identifiziert. Angaben über die spezifischen Retentionsvolumina an einer Apiezon-K-Säule werden für eine Anzahl von Methacrylsäureestern von geradkettigen Alkoholen im Bereich von C<sub>2</sub> bis C<sub>18</sub> gemacht. Verfahren zur Voraussage der Retentionsvolumina von unbekanntem Methacrylsäureestern bei beliebiger Temperatur werden beschrieben. Die Methode verspricht für die Analyse von Copolymeren aus einer grossen Reihe von Vinylmonomeren brauchbar zu sein.

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