

Highly Precise Quantitative Gas Chromatographic Method and Its Application to the Determination of Copolymerization Kinetics

Anton L. German and Derk Heikens

Laboratory of Polymer Technology, Eindhoven University of Technology, The Netherlands

When using commercial gas chromatographs as well as specially built equipment, the precision of analysis is mostly of the order of magnitude of a few percent. A study focused on those parameters that affect the precision in gas chromatography, analogous to the investigation of Goedert and Guiochon, has led to the development of a system of such precision as to become suitable for a detailed determination of copolymerization kinetics. This attainment is of paramount importance in polymer chemistry, the more so as the procedures generally used to study copolymerization reactions are deficient in achieving the precision required. The present technique, which easily permits frequent and representative sampling from a pressure vessel throughout chemical processes, has been applied to the free-radical ethylene-vinylacetate copolymerization in solution at 35 kgf/cm² (= 33.9 atm) and 62 °C. A matching computational procedure guarantees efficient use of the resulting extensive information.

GAS CHROMATOGRAPHY has been used incidentally (1, 2) in support of the study on copolymerization kinetics. However, the techniques in question are still dovetailed into the conventional methods of determining the monomer reactivity ratios [discussed by Tidwell and Mortimer (3, 4)] and yield only little information, *i.e.*, initial (intermediate or final) feed composition, per kinetic series. In addition, the common methods do not allow high precision in sampling and analysis, and fail when gaseous monomers (*viz.*, high pressures) are involved.

The new gas chromatographic technique described in this paper allows a detailed study on the *course* of copolymerization reactions up to 20–40% conversion and affords high precision in determining *r*-values and thus in model testing. The advantages of the present method include the omission of copolymer analysis with its accompanying errors. When gaseous monomers are involved, the method is particularly favorable.

PRINCIPLES OF OPERATION

A diagram of the equipment is shown in Figure 1. The reactor is a vertically placed cylindrical stainless steel vessel provided with a piston. The upper compartment (approx. 750 cm³) serves as reaction chamber and initially contains both monomers ethylene and vinylacetate, the solvent *tert*-butylalcohol (TBA), and the radical initiator α,α' -azodiisobutyronitrile. The lower compartment permits pressure control. This type of reactor (5) guarantees the absence of a gas phase,

operation at constant pressure, and easy representative sampling.

By means of a disk valve, samples of constant volume (5 μ l) are taken from the reactor every 10 minutes during 4–6 hours and introduced into a gas chromatograph. The samples remain under reaction conditions (35 kgf/cm² = 33.9 atm and 62 °C) until the very moment of expansion and vaporization in the carrier gas stream of the gas chromatograph. Copolymer present in the sample is retained by a precolumn. The peak areas of the three remaining components, ethylene (A_e), vinylacetate (A_v), and TBA (A_b), are determined by electronic integration of the catharometer signal.

The analytical system is calibrated by injecting, by means of the same sampling device, reference samples of the pure monomers ethylene and vinylacetate (relevant peak areas A_{er} and A_{vr}) which have well known densities (c_{er} and c_{vr}) under the appropriate conditions.

In this way, a number of experiments are carried out starting from different monomer feed compositions.

EQUIPMENT

Sampling Device. The first step in the analysis is sampling from the reactor, which is at a pressure of 35 kgf/cm². At this pressure level, a sampling repeatability range of 0.1% is required at a sample size of the order of magnitude of some microliters.

The principles of the sampling valve are shown in Figure 2. The valve body contains two channels of 1.5 mm i.d. One of these is incorporated in the carrier gas system of a gas chromatograph, the other is connected to the sample tube emerging from the reactor. The two plastic sealing rings (B in Figure 2) are attached to the valve body by means of rods. The steel disk (A in Figure 2) can be turned between the two sealing rings by means of the shaft (J in Figure 2). The steel disk is provided with six bores, one of them forming the sample volume. By turning the disk over 60°, the volume of the bore (5 μ l) is introduced into the carrier gas stream.

A requirement of the sampling valve is to be gas-tight at 40 kgf/cm². To ensure a reasonable operating torque at the necessary sealing pressure, the sealing materials to be applied must exhibit: low static friction, low dynamic friction, low stress relaxation, high scratch resistance, and good sealing properties. Sealing materials for these purposes have been developed during this research based on Kel F-Teflon-Molykote composites.

It is essential that the sample in the sampling valve is under the conditions of temperature and pressure of the reactor. Any temperature or pressure difference may cause phase separation and thus decrease sampling accuracy. For these reasons, the sampling valve is placed in an air bath kept at 62 \pm 0.05 °C. Moreover, restrictions between the reactor and the sampling valve are avoided and flushing of the sampling system takes place by means of a needle valve situated behind the sampling valve.

In the carrier gas stream between the sampling valve and the gas chromatograph, a precolumn is placed, 3 cm long and 1/4 in. in o.d., packed with glass fiber and controlled

- (1) A. Guyot and J. Guillet, *J. Chim. Phys.*, **61**, 1434 (1964).
- (2) E. B. Mano and R. Riva de Almeida, *J. Polymer Sci. A-1*, **8**, 2713 (1970).
- (3) P. W. Tidwell and G. A. Mortimer, *J. Polymer Sci. A*, **3**, 369 (1965).
- (4) P. W. Tidwell and G. A. Mortimer, *J. Macromol. Sci.*, **C4**, 281 (1970).
- (5) A. L. German, Thesis, Eindhoven University of Technology, (1970).

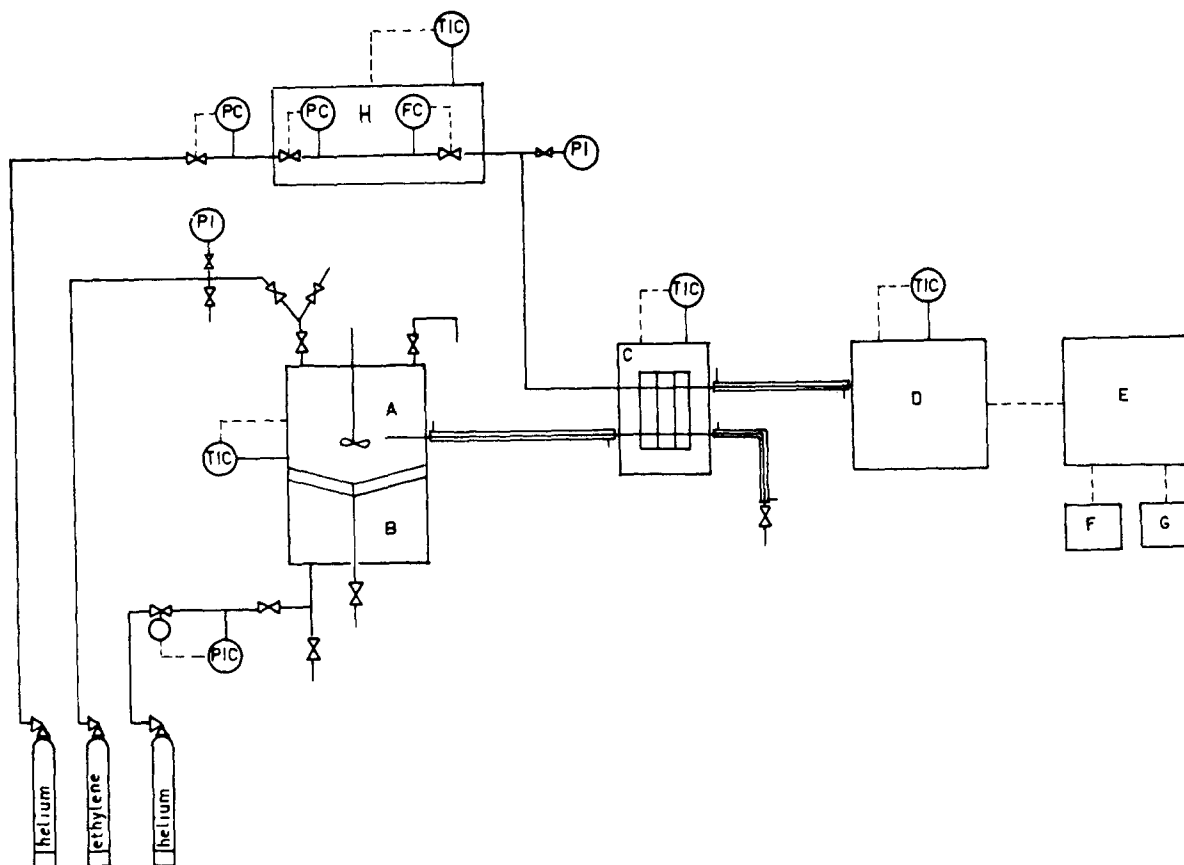


Figure 1. Simplified scheme of integral equipment

TIC = temperature indicator controller
 PI(C) = pressure indicator (controller)
 PC = pressure controller
 FC = flow controller

A = reactor
 B = compartment for pressure control
 C = sampling device
 D = gas chromatograph

E = electronic integrator
 F = recorder
 G = digital printer
 H = pressure and flow controllers

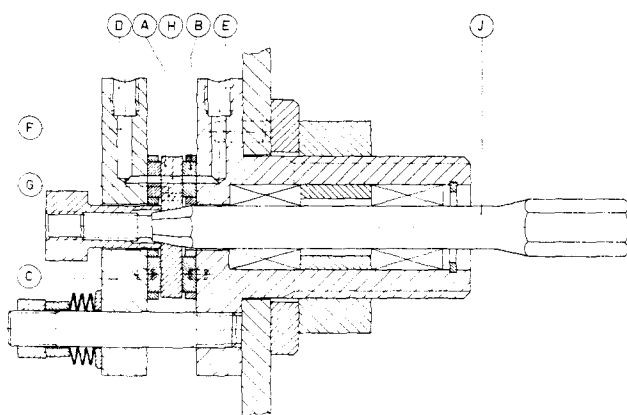


Figure 2. Sampling valve

A = steel disk
 B = plastic sealing ring
 C = valve body
 D = sample inlet
 E = sample outlet
 F = sample channel
 G = carrier gas channel
 H = sample chamber
 J = spindle

at 75 ± 0.1 °C. The precolumn is used to retain the very small amounts of polymer from the injected samples and to vaporize the liquid components.

Gas Chromatograph. The gas chromatograph used is a modified Hewlett-Packard (F & M Scientific Division) Model 720, in which all control systems have been replaced

by more accurate controllers to meet the precision claimed. High precision in temperature controlling is achieved, using proportional temperature controllers with adjustable integral and derivative action (Eurotherm type PID/SCR-10).

A typical chromatogram is shown in Figure 3 and the experimental conditions of the gas chromatograph are listed in Table I.

Electronic Integrator. In order to determine the peak areas, the detector output is connected to an electronic integrator (Infotronics type CRS-100 or CRS-110). It appeared that electronic integrators may exhibit considerable deviations from linearity. To regard the linearity of electronic integrators as a reliable feature merely because it cannot simply be verified, appears very dangerous. In behalf of the research described in this paper, a comparatively simple method has been applied to check the linearity of the integrators.

PRECISION OF ANALYSIS

Both monomers and the solvent were shown to be stable under the gas chromatographic conditions.

Repeatability. The peak area determined by integration of the detector signal is given by the following equation (6):

(6) M. Goedert and G. Guiochon, "Advances in Chromatography," Proceedings of the Fifth International Symposium, Las Vegas, 1969, Preston Technical Abstracts Company, Evanston, Ill.

Table I. Experimental Conditions of the Gas Chromatographic System

Column	3-Meter stainless steel coiled tubing 1/4-in. o.d.
Solid support	Chromosorb G 60-80 mesh (acid washed and treated with dimethylchlorosilane) Hewlett-Packard
Stationary phase	10% by weight of a mixture of diglycerol and Carbowax 400 (60/40% by weight)
Carrier gas	Helium dried over Linde Molecular Sieves (type 5 A, 1/8-in. pellets)
Flow control	Accomplished by the combined action of the following devices connected in series in the order as indicated (all pressures are absolute): Reducing valve on cylinder, 200-5 kgf/cm ² ; Reducing valve (Negretti) at room temperature, 5-4 kgf/cm ² ; Reducing valve (Negretti) thermostatically controlled at 25 ± 0.05 °C, 4-3 kgf/cm ² ; Flow controller (Brooks Model 8743), thermostatically controlled at 25 ± 0.05 °C, flow rate 1 cm ³ /sec Column inlet pressure: 1.5 kgf/cm ² Column outlet pressure: atmospheric
Column temperature	75 ± 0.05 °C
Detector	Heat conductivity cell (Gow-Mac, semi-diffusion type) temperature 108 ± 0.05 °C
Bridge current	150-200 mA, current stabilization by means of a dc power supply unit (Hewlett-Packard Type 6112A)
Injection mode	The sample is injected directly into the pre-column, which also serves as vaporizing chamber. The precolumn as well as the tube (1/8-in. o.d.) connecting it with the gas chromatographic column is kept at 75 ± 0.1 °C
Integrator	Base-line tracking up 0.1 μV/sec Base-line tracking down 1 μV/sec Slope sensitivity 0.3 μV/sec

Table II. Survey of Various Factors Affecting Peak Area Repeatability Range

Factor	Affected parameter in Equation 1	Influence on peak area repeatability ^a	
		Short-term changes, <2 hours, %	Long-term changes, 0-12 hours, %
Sample size	M	0.1	0.1
Column oven temperature	D	<0.1	0.2
Carrier gas flow rate	D	<0.1	0.3
Detector sensitivity	S	<0.1	0.2
Integrator	k^b	0.2 ^b	0.2 ^b
	k^c	0.6 ^c	0.6 ^c
Total repeatability range for the determination of a peak area		0.25 ^b 0.6 ^c	0.5 ^b 0.75 ^c

^a A repeatability range of $x\%$ denotes that 90% of all observations lie between $+1/2x\%$ and $-1/2x\%$ from the mean value.

^b For ethylene and vinylacetate peaks.

^c For TBA peaks.

$$A = k \frac{S}{D} M \quad (1)$$

with A = peak area

k = constant for gas chromatograph and integrator combination

S = detector sensitivity

D = mass flow rate of carrier gas

M = total mass of one component from the sample

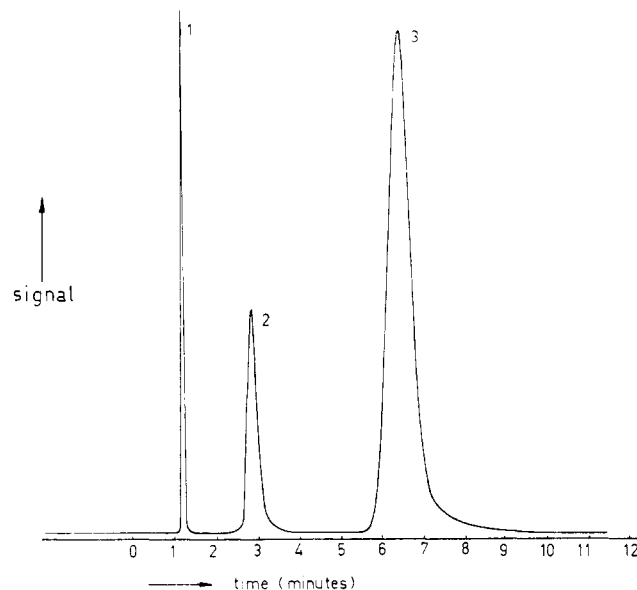


Figure 3. Typical chromatogram

1 = ethylene, 2 = vinylacetate, and 3 = *tert*-butylalcohol. Conditions are given in Table I

The detector sensitivity S depends on the bridge current I (6):

$$\frac{dS}{S} = 3 \frac{dI}{I}$$

Table II lists the estimated contributions of the different factors to the measured peak area repeatability range.

The possibility of carrying out gas chromatography with the precision claimed, under the relevant conditions, is confirmed by Goedert and Guiochon (6).

Linearity of the Analytical System. As the composition of the monomer feed and the degree of conversion will be calculated by Equations 2 and 3, the linearity of the integral analytical system has to be investigated. The results are given in Table III.

Within one kinetic series the estimated mean value of the error due to nonlinearity is 0.2% for the determination of ratios of peak areas from the same component.

EXPERIMENTAL DATA

In behalf of the computation of the monomer reactivity ratios, the molar feed ratio $q = n_e/n_v$ (n_e and n_v are numbers of moles of ethylene and vinylacetate, respectively, in the reactor) and the degree of conversion f_v (based on vinylacetate) has to be calculated from the measured peak areas, for any one sampling.

The relations concerned are given by:

$$q = \frac{n_e}{n_v} = \frac{A_e \times A_{vr} \times c_{er}}{A_v \times A_{er} \times c_{vr}} \quad (2)$$

and

$$f_v = 100 \left\{ 1 - \frac{A_v \times (A_b)_0}{A_b \times (A_v)_0} \right\} \% \quad (3)$$

where the subscript zero denotes the conditions at zero conversion.

There are some important considerations about Equations 2 and 3:

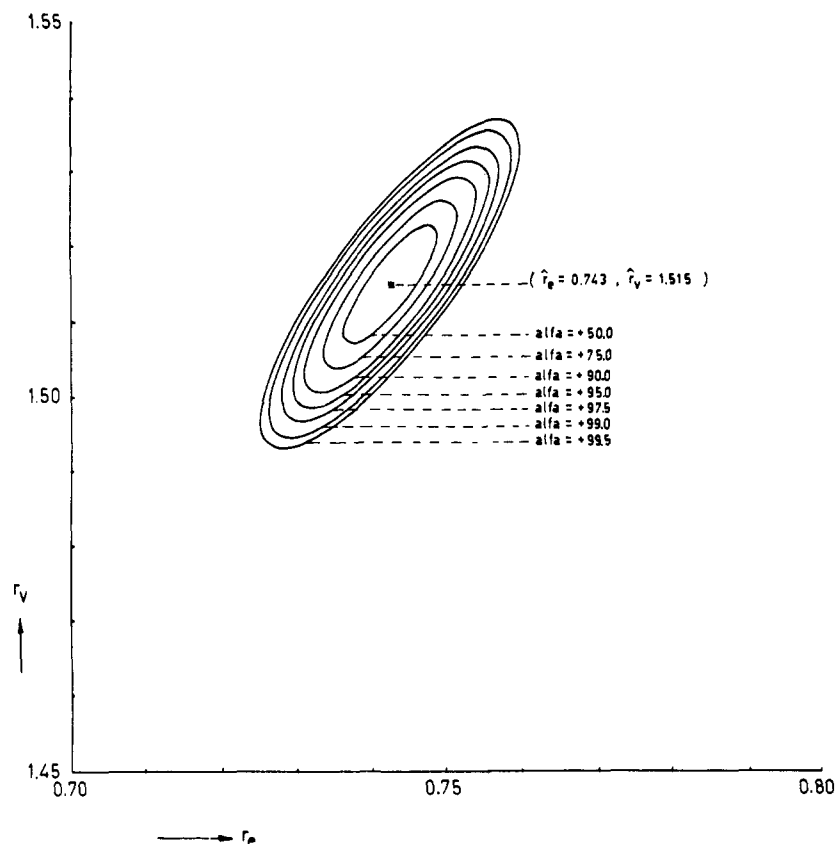


Figure 4. Confidence regions, derived from the F.C.A. method

\hat{r}_e (ethylene) and \hat{r}_v (vinylacetate) are the least-squares estimates for the monomer reactivity ratios r_e and r_v , and α = probability level

Table III. Factors Affecting Linearity of Analytical System

Factor	Nonlinearity, % ^a	Region	Remarks
Pressure dependence of sample size	1.2	1–35 kgf/cm ²	Irrelevant if all samples are taken at the same pressure level
Integrator	0.25	0.1–60 mV input signal	Investigated by integration of block functions
Detector	0.2	Quantities to be detected varying from 1.5×10^{-6} to 50×10^{-6} mole; Peak crest concentrations varying from 0.5–5 mole % in the carrier gas	Determined by injecting such amounts of ethylene and such compositions of vinylacetate/TBA mixtures as to cover the region mentioned
Peak separation	0.1	All experiments	Complete base-line recovery between all peaks

^a Nonlinearity $x\%$ means: the maximum deviation from linearity in the region indicated is $+1/2 x\%$ or $-1/2 x\%$, the middle of the region having deviation zero by definition.

As A_e/A_v , A_v/A_b , and $(A_b)_0/(A_v)_0$ are ratios of peak areas resulting from any one sampling, these quantities are nearly independent of the error sources listed in Table II, except for the repeatability range of the integrator.

The value of f_v is independent of sample size; once the reference samples have been injected, $q = n_e/n_v$ becomes independent of sample size.

The error in A_{er}/A_{vr} due to nonrepeatability only depends on the peak area repeatability range on short term (see Table II), if the reference injections are carried out within an interval of 1.5 hours.

The value of A_{er}/A_{vr} appears to be constant $\pm 0.3\%$ during a period of approximately one year. Since the calculations of *all* experiments are performed with the average value of $A_{er}/A_{vr} = 0.08254$, this ratio does not contribute to the random error in $q = n_e/n_v$.

Also the ratio c_{er}/c_{vr} = constant does not contribute to the random error in $q = n_e/n_v$.

These considerations, together with the data from Table III lead to the conclusion that the estimated mean error in the determination of $q = n_e/n_v$ is $\pm 0.2\%$ and of f_v is $\pm 0.4\%$ (conversion), both at 90% confidence level.

EVALUATION OF RESULTS

A generally accepted model describing the free-radical copolymerization is given by Mayo and Lewis (7) and Alfrey and Goldfinger (8). For any conversion interval $0-f_v$ (based on vinylacetate) the integrated form (7, 9, 10) of their copolymer equation can be formulated briefly as:

$$F(r_e, r_v, q_0, q, f_v) = 0 \quad (4)$$

where r_e (ethylene) and r_v (vinylacetate) are the monomer reactivity ratios to be determined and the subscript zero indicates the conditions at zero conversion.

The "Feed Compositional Analysis Method." The experimental method described in this paper affords approximately 25 experimental data pairs per high-conversion copolymerization experiment. The substantially increased number of experimental data per kinetic series allows, as compared with the conventional methods, a more precise evaluation of the monomer reactivity ratios. The computational procedure summarized here takes advantage of the extended amount of information and will be referred to as the "Feed Compositional Analysis (F.C.A.) method."

In the present investigation, the experimental data are available, according to Equations 2 and 3, as a series of values $q_i = (n_e/n_v)_i$, describing the monomer feed composition at corresponding degrees of conversion $(f_v)_i$ for any kinetic experiment. Thus each kinetic series ($k = 1, \dots, n$), producing g_k data pairs $(q_{ik}, (f_v)_{ik})$, yields g_k conversion intervals $0-(f_v)_{ik}$ and consequently g_k equations F_{ik} (Equation 4):

$$F_{ik} = F[r_e, r_v, q_{0k}, q_{ik}, (f_v)_{ik}]$$

with $i = 1, \dots, g_k$; g_k = number of input data pairs resulting from the k th experiment

$k = 1, \dots, n$; n = number of kinetic series

F_{ik} represents (5) the difference between the measured degree of conversion $(f_v)_{ik}$ and the corresponding calculated expression for the degree of conversion; (q_{0k} is the intercept on the q axis of the q vs. f_v relation for any kinetic series). Owing to the random experimental error, generally $F_{ik} \neq 0$ for any r_e, r_v , and q_{0k} combination. Now, the combined information resulting from all kinetic experiments (221 data pairs) gives ample information to determine the least-squares estimates for r_e, r_v , and q_{0k} by selecting those values of r_e, r_v , and q_{0k} that minimize:

$$\sum_{k=1}^n \sum_{i=1}^{g_k} F_{ik}^2 [r_e, r_v, q_{0k}, q_{ik}, (f_v)_{ik}]$$

For the solution of this nonlinear least-squares method (5), a computer program in Algol 60 is available upon request.

RESULTS

The above minimization procedure immediately leads to the least-squares estimates for r_e, r_v , and q_{0k} , and also the standard deviations and confidence regions (Figure 4) can be calculated (10):

$$\hat{r}_e = 0.743 \pm 0.005$$

$$\hat{r}_v = 1.515 \pm 0.007$$

In addition, it has been proved statistically (5) that the Mayo-Alfrey model is completely supported by the data obtained under the relevant conditions within the narrow limits imposed by the experimental error.

CONCLUSIONS

Even under more complicated reaction conditions (pressure, gaseous monomer, presence of copolymer), an excellent sampling repeatability can be obtained with the aid of the given sampling device. In accordance with the important results of Goedert and Guiochon (6), the present investigation indicates that proper control of the analysis conditions renders it possible to achieve a high level of precision in quantitative gas chromatography.

Furthermore, the error in the determination of the kinetic parameters (q, f_v) chosen here is substantially reduced as several error contributions occurring in the individual peak areas cancel out.

The main feature of the improved experimental approach described in this paper is that it leads to an extended accessibility of the characteristic variables (q, f_v) through precise sequential analysis of unreacted monomer rather than isolated copolymer composition. The relevant method does not show any of the disadvantages of the usual methods and allows a more justified and precise determination of the monomer reactivity ratios. The latter is of paramount importance for model testing and for the future research on the influence of pressure on copolymerization kinetics, as relatively small effects are to be expected.

ACKNOWLEDGMENT

The authors acknowledge A. I. M. Keulemans, Director of the Department of Instrumental Analysis of the Eindhoven University of Technology, for his supportive interest in the development of the pertinent technique and the enhancement of the precision in gas chromatography.

RECEIVED for review July 12, 1971. Accepted August 30, 1971.

- (7) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
- (8) T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).
- (9) D. R. Montgomery and C. E. Fry, *J. Polymer Sci. C*, **25**, 59 (1968).
- (10) D. W. Behnken, *J. Polymer Sci. A*, **2**, 645 (1964).