

# Effect of pressure on free radical copolymerization kinetics. II. Novel methods of measuring monomer reactivity ratios under high-pressure conditions

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# Effect of Pressure on Free Radical Copolymerization Kinetics. II. Novel Methods of Measuring Monomer Reactivity Ratios under High-Pressure Conditions

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## Synopsis

Two new techniques for the determination of monomer reactivity ratios in copolymerization under high-pressure conditions have been developed, viz., the "sandwich" and the "quenching" method. Both methods are based on repeated quantitative gas chromatographic analysis of the reaction mixture during the low-pressure stages preceding and succeeding the high-pressure stage, of which the kinetics is under investigation. Application of the "sandwich" method implies the occurrence of reaction during both low-pressure stages and consequently the low-pressure kinetic data are required to obtain the transition points of low to high pressure and vice versa. These points constitute the initial and final conditions of the relevant high-pressure reaction. On the contrary, in the "quenching" method no reaction occurs during the low-pressure stages, owing to the lower temperature and the high activation energy of the initiator decomposition. As a consequence, the initial and final conditions of the high-pressure stage can be determined by a simple averaging procedure. Both methods have been tested for the ethylene-vinyl acetate copolymerization at 62°C and 600 kg/cm<sup>2</sup> with *tert*-butyl alcohol as solvent, and appear to lead to almost identical monomer reactivity ratios, although the "quenching" method is slightly preferred in case of copolymerization reactions. Both methods are particularly valuable when one of the reactants is gaseous or the reaction produces a gas. Further merits and drawbacks of both methods are discussed.

## INTRODUCTION

The application of quantitative gas chromatographic analysis for the determination of monomer reactivity ratios in copolymerization has been reported by many investigators.<sup>1-6</sup> A direct measurement of the changing monomer feed composition has many advantages in comparison with the conventional procedures where laborious and inaccurate copolymer isolation, purification, and compositional analysis were necessary.<sup>7</sup>

By means of the gas-liquid chromatographic (GLC) technique the course of a copolymerization reaction can be studied up to a high degree of conversion (ca. 40%). This method allows an objective test of the proposed mathematical model,<sup>8</sup> e.g., the simple copolymer equation of Alfrey and Mayo.<sup>9,10</sup> German and Heikens<sup>5</sup> have reported an application of the GLC technique, permitting direct sampling from the reaction mixture up to pressures of about 40 kg/cm<sup>2</sup>, by means of a specially constructed sampling device.<sup>11</sup> This technique is particularly useful when gaseous monomers are involved in the copolymerization reaction.

Although direct sampling from reaction mixtures under high pressure has been shown to be possible,<sup>12,13</sup> the application of on-line GLC analysis under these conditions is still to be achieved. In our laboratory two alternative procedures

have been developed both based on repeated quantitative GLC analysis of the reaction mixture just preceding and succeeding the relevant high-pressure copolymerization reaction. Both techniques have in common that samples are taken directly from the reaction mixture under low-pressure conditions. In the "sandwich" method sampling takes place from a copolymerizing reaction mixture, whereas in the "quenching" method no reaction occurs at the moment the samples are taken. In our previous article,<sup>14</sup> dealing with the effect of pressure on copolymerization kinetics, the necessity of precise determination of relatively small effects has been shown. Consequently, a critical evaluation of the experimental methods presently developed, is imperative.

## EXPERIMENTAL

### Reagents

The physical properties and the quality of the reagents ethylene (Eth), vinyl acetate (VAc), *tert*-butyl alcohol (TBA), and  $\alpha,\alpha'$ -azobisisobutyronitrile are identical to those given earlier.<sup>5</sup>

### Apparatus

A block diagram of the high-pressure reaction system and its main components is shown in Figure 1. The gas chromatographic system used is the same as described previously.<sup>11</sup>

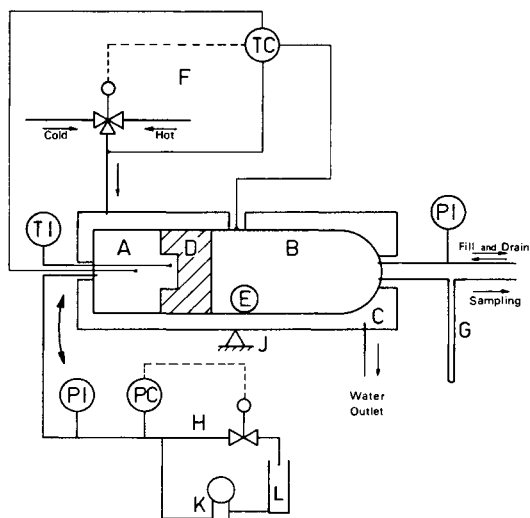


Fig. 1. A, compartment connected with pressure control system; B, reaction chamber; C, heating jacket; D, Teflon piston; E, Teflon coated lead ball; F, temperature control system; G, cryogenic capillary hairpin valve; H, pressure control system; J, rocking point of the reactor; K, diaphragm pump; L, supply flask. Simplified scheme of the high-pressure apparatus used in the present investigation.

## HIGH-PRESSURE REACTOR

The high-pressure experiments have been carried out in a modified version of an Autoclave Engineers autoclave type No. 261575Z, manufactured from stainless steel A 286. At 62°C, the maximum working pressure is 2500 kg/cm<sup>2</sup>. The approximate volume of the system amounts 500 ml, and the reaction volume of the cylinder is approximately 300 ml. The reactor is provided with an external cylindrical heating jacket through which water is circulated from a thermostat.

The vessel is operated as a closed reaction system containing liquid phase only. By means of the Teflon piston, the reaction chamber is separated from a compartment filled with isopropyl alcohol, which compartment is connected with a pressure control system, as shown in Figure 1. The reactor is rocked throughout the copolymerization reaction, so that the reaction mixture is stirred by the movement of a Teflon-coated lead ball inside.

The reaction temperature is measured by means of a coaxial iron-constantan thermocouple.

### Temperature Control

Owing to the heavy stainless steel wall of the high-pressure reaction vessel, the temperature response of the contents of the reactor to temperature changes of the water flowing through the jacket is severely delayed. The "sandwich" method, in particular, demands a very rapid and adequate temperature control at the transition from low to high, and high to low pressure. Temperature overshoot should be prevented as much as possible, since the resulting volume changes will lead to a decrease of pressure stability, and lead to systematic errors in the calculated monomer reactivity ratios.

Satisfactory results are achieved with a system consisting of (a) two thermostat baths, both filled with water: one at a temperature of approximately 75°C, and one at approximately 45°C; (b) an electronically controlled three-way valve, mixing the streams from the thermostats; (c) three temperature sensors (quartz-sheathed Pt-100 resistance thermometers), successively placed in the reaction chamber, the reactor wall, and the supply pipe, just behind the mixing valve. Their respective signals are fed into a servo-amplifier, with the signal of the reactor sensor as "master signal" and the other two as individual and combined variable feedback signals.

By careful adjustment of gain and negative feedback, a precision of ca. 0.2°C at a reaction temperature of 62°C has been achieved, except at the above-mentioned points of transition in the "sandwich" method where temperature fluctuations can only be minimized to ca. 1°C.

### Pressure Control

A fast-responding and accurate pressure control system has been assembled from the following components: a high-pressure diaphragm pump with remotely controllable piston stroke, type Lewa HM-1; a Foxboro-type M/45 pneumatic pressure transmitter equipped with a type 250 heavy-duty helical pressure element; a Foxboro Consotrol model 52A pneumatic controller with adjustable proportional and integral action; and a pneumatically actuated Annin model 5060 "Wee Willie" Domoter valve.

Pressure is transmitted by isopropyl alcohol. The system is optimized by adjusting the pump piston stroke and the proportional and integrating action of the controller. A precision of ca. 0.5 kg/cm<sup>2</sup> at 35 kg/cm<sup>2</sup>, and ca. 5 kg/cm<sup>2</sup> at 600 kg/cm<sup>2</sup> is obtained.

## SAMPLING SYSTEM

The disk valve used in this investigation has been described elsewhere.<sup>11</sup> During the high-pressure stages of both the "sandwich" and the "quenching" experiments the disk valve is guarded against the high pressure in the reactor by a stainless steel "cryogenic capillary hairpin" having a 2 mm i.d. The liquid in this hairpin is solidified by immersion in liquid nitrogen and blocks the passage. In this manner dead volumes present in regular high-pressure valves are avoided.

### Introduction of Components into the Reactor

First the reaction chamber and the compartment for pressure control are heated up to the desired temperature level and evacuated. The pressure transmitting liquid is sucked into the pressure control system by the vacuum. Next, ethylene gas is admitted from a gas cylinder into the reaction chamber up to a pressure, empirically related to the desired quantity of Eth in the reaction mixture. Then a mixture of the solvent TBA, and VAc, that contains the radical initiator is pumped into the reaction chamber by the diaphragm pump. Next, isopropyl alcohol is pumped into chamber A (see Fig. 1) until a pressure of about 60 kg/cm<sup>2</sup> is reached. This pressure is maintained for 1/2 hr to ensure that all Eth has dissolved. Then pressure is reduced to the low-pressure conditions for sampling (35 kg/cm<sup>2</sup>).

### Sampling

In previous articles<sup>5,11</sup> details have been given on our experimental method of "sequential sampling" throughout the copolymerization reaction under low-pressure conditions.

However, direct sampling for GLC under high-pressure conditions is not yet possible. Therefore, we resorted to the "sandwich" and "quenching" methods where gas chromatographic observations prior to and after the relevant high-pressure stage can be performed under low-pressure conditions. In both procedures we will distinguish three succeeding pressure levels, viz., stages A, B, and C during each complete copolymerization experiment, as shown in Figure 2.

### "SANDWICH" METHOD

In this procedure the reaction is started in stage A, at 35 kg/cm<sup>2</sup> and 62°C, where the course of the reaction is followed by means of GLC observations. As soon as a degree of conversion of about 10% is reached, the reaction chamber is shut off from the disk valve, and the pressure is raised to the desired high-pressure level (600 kg/cm<sup>2</sup> in this investigation).

During the high-pressure stage (B) the copolymerization is allowed to proceed another 20–30%. An exact degree of conversion, however, is not known during

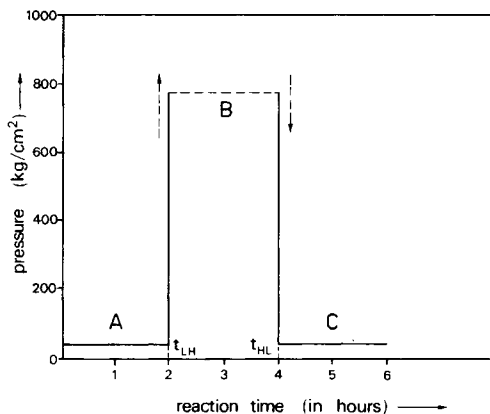


Fig. 2. Graphical representation of the successive pressure levels appearing during both a “sandwich” and a “quenching” experiment.

this stage, because no GLC observations can be made. Then, at  $t_{HL}$  the pressure is decreased again to the previous low level (stage C) where a new set of GLC observations of the copolymerizing reaction mixture can be made.

The monomer feed ratio ( $q$ ) at the moment of transition from low to high pressure ( $t_{LH}$ ) and from high to low pressure ( $t_{HL}$ ) can be obtained by extrapolating the observed  $q$ , during the initial stage A, and during the final stage C, in a  $q-t$  diagram, to the times of transition [see Fig. 3 (II)]. In this manner a fairly good estimate of the initial and final conditions of the high-pressure reaction is obtained. Performance of a set of 10–15 “sandwich” experiments enables calculation of reliable high-pressure monomer reactivity ratios.

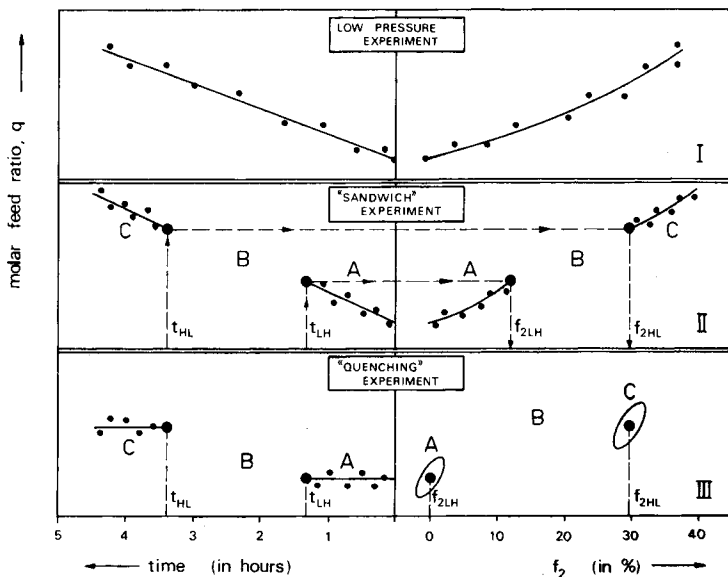


Fig. 3. Plots of the monomer feed ratio versus both the reaction time and the degree of conversion for (I) a complete low-pressure experiment, (II) a “sandwich” experiment, and (III) a “quenching” experiment.

### “QUENCHING” METHOD

In this procedure, besides different pressure levels (see Fig. 2), different temperature levels also have to be distinguished. During the low-pressure stage A at 35 kg/cm<sup>2</sup> and a temperature of approximately 50°C the initiator decomposition is proceeding only very slowly, and this has the desired effect of lengthening the induction period which occurs in the radical copolymerizations studied. Under those conditions the monomer feed composition remains constant and can be determined accurately by making a large number of GLC observations.

Before the copolymerization reaction starts both pressure and temperature are raised to the desired higher level (600 kg/cm<sup>2</sup>, 62°C). As soon as a degree of conversion of ca. 30% has been reached in stage B (a matter of estimation by experience), pressure and temperature levels are lowered simultaneously. A quick decrease of temperature to ca. 30°C can be achieved easily by circulating cold tap water. The heat of compression and decompression at the transition points also facilitates the required temperature changes.

Because of the very slow decomposition rate of the radical initiator in stage C, owing to its high activation energy of decomposition,<sup>15</sup> the composition of the reaction mixture does not change noticeably after quenching, as shown schematically in Figure 3 (III), and another set of GLC observations can be made.

The monomer feed composition at the start and the end of the high-pressure reaction can be determined simply by averaging the observations of stages A and C, respectively.

### ESTIMATION OF MONOMER REACTIVITY RATIOS

Recently we developed the (improved) curve-fitting I procedure for the evaluation of monomer reactivity ratios in copolymerization.<sup>16</sup> This computational procedure starts from the integrated copolymer equation, while experimental errors in both variables, viz., the degree of conversion, based on  $M_2$ ,  $f_2 = 100(1 - n_2/n_{20})\%$ , and the molar feed ratio  $q = n_1/n_2$  are considered. In the latter expressions  $n_1$  and  $n_2$  are the numbers of moles of monomer  $M_1$  and  $M_2$ , respectively, and the subscript zero denotes initial conditions.

The application of this minimization procedure will be explained below for both the “sandwich” and the “quenching” method with the help of Figure 3, which shows curves of the molar feed ratio versus the degree of conversion and versus the reaction time for (I) a complete low-pressure experiment, (II) a “sandwich” experiment, and (III) a “quenching” experiment.

#### “Sandwich” Method

Each kinetic experiment covers two low-pressure stages (A and C). Monomer reactivity ratios from those “2n” experiments can be estimated by means of the curve-fitting I procedure,<sup>16</sup> taking into account relative measurement errors in the GLC peak areas of Eth ( $M_1$ ), VAc ( $M_2$ ), and TBA of 1.0%, 1.0%, and 1.5%, successively. This yields the best-fitting curves for all observations, so that  $f_{2LH}$  and  $f_{2HL}$  can easily be calculated, as  $q_{LH}$  and  $q_{HL}$  are known. The latter quantities are determined by extrapolation of  $t$  vs.  $q$  ( $t_{LH} \rightarrow q_{LH}$  and  $t_{HL} \rightarrow q_{HL}$ ). An exact relation describing the change of the monomer feed ratio ( $q$ ) as a function

of time is very complex,<sup>17,18</sup> however, for a small conversion range a first-order polynomial is a satisfactory approximation.<sup>18</sup>

In the present investigation this approximation has been used for the calculation of the transition points. As, in principle, the high-pressure stage of each kinetic experiment ( $j = 1, \dots, n$ ) starts at a different degree of conversion  $f_{2LHj}$ , it is necessary to transform  $f_{2HLj}$ . Transformation of  $f_{2LHj}$  to  $f'_{2LHj} = 0$  easily leads to an expression for  $f'_{2HLj}$ :

$$f'_{2HLj} = 100 \left( 1 - \frac{100 - f_{2HLj}}{100 - f_{2LHj}} \right) \%$$

For each "sandwich" experiment only two observations relevant to the high-pressure stage of the copolymerization are obtained, viz., the start of the high-pressure reaction ( $q_{LH}, f'_{2LH} = 0$ ), and the end of the high-pressure reaction ( $q_{HL}, f'_{2HL}$ ). In other words  $n$  experiments lead to  $2n$  observations, and, in principle, calculation of the  $n + 2$  unknown parameters [ $r_1, r_2, q_{0j}$  ( $j = 1, \dots, n$ )] can be achieved for  $n \geq 2$ . However, the occurrence of experimental errors calls for more experiments in order to calculate sufficiently accurate monomer reactivity ratios.

Then the computation of the high-pressure parameters has been carried out by means of the curve-fitting I procedure, although it is debatable if the error structure of the transition points completely corresponds with the errors of the separate GLC observations in the stages A and C. Nevertheless, it has been assumed that this is the case.

### "Quenching" Method

In this method a series of GLC analyses of the reaction mixture is made in stage A, before the high-pressure reaction is started. The same is done in stage C, after the high-pressure stage B. Since conversion occurs neither in stage A nor in stage C, all GLC observations in each stage separately, should be identical within experimental error. As a result the degree of conversion at  $t_{LH}$  is equal to zero.

In Figure 3 (III) two elliptical curves are shown, enclosing the error region of the GLC observations resulting from stages A and C. This shape occurs because  $q$  and  $f_2$  both contain the experimental error associated with measurement of the number of moles of  $M_2$  ( $n_2$ ). Calculation of the high-pressure reactivity ratios can then be achieved according to two basically different procedures:

(a) The observations of stages A and C separately are averaged leading to  $(q_{LHj}, f_{2LHj})$  and  $(q_{HLj}, f_{2HLj})$ , respectively, where  $f_{2LHj} = 0$ . Then the high-pressure monomer reactivity ratios can be calculated completely analogous to the way discussed above for the "sandwich" method.

(b) Without averaging, all separate observations are used simultaneously for the estimation of the high-pressure monomer reactivity ratios by means of the curve-fitting I procedure.<sup>16</sup>

In method (b) each observation is equally weighted, whereas in method (a) the averaged values should be assigned a "weight" dependent on the number of observations obtained within the relevant stage. Therefore, method (b) should be preferred. The procedures (a) and (b) will only lead to identical results when all kinetic experiments contain an equal number of observations while, furthermore, the observations should be equally distributed between the stages A and C.



In the following section both procedures (a) and (b) are used to calculate the monomer reactivity ratios, and the results are compared.

As all observations within each separate stage of a "quenching" experiment should contain the same information, this method offers the possibility to arrive statistically at a more reliable estimation of the variances of  $q$  and  $f_2$  than by estimating the relative errors in the peak areas of both monomers and the solvent. Use of these variances in the curve-fitting I procedure appears to lead to results identical to those resulting from method (b) (within the pertaining standard deviations).

## RESULTS AND DISCUSSION

The practical use of the "sandwich" and "quenching" method has been tested for the Eth-VAc copolymerization at 600 kg/cm<sup>2</sup> and 62°C, with TBA as solvent. A total of 12 "sandwich" experiments have been performed with varying initial monomer feed composition. Further details on these experiments are summarized in Table I. Monomer reactivity ratios calculated on the basis of these experiments are  $r_1 = 0.79 \pm 0.015$  and  $r_2 = 1.40 \pm 0.02$ .

A total of 13 "quenching" experiments have been performed. The experimental details of these kinetic runs are summarized in Table II. Calculation of the high-pressure monomer reactivity ratios based on procedure (a) (averaged observations) yields  $r_1 = 0.795 \pm 0.015$  and  $r_2 = 1.43 \pm 0.02$ , while the use of procedure (b) gives  $r_1 = 0.776 \pm 0.007$  and  $r_2 = 1.42 \pm 0.015$ .

Although the reactivity ratios obtained from the "sandwich" and "quenching" methods are not identical, their standard deviations overlap. From Figure 4, in which the confidence regions of the monomer reactivity ratios resulting from both experimental methods are shown, it may be concluded that any systematic deviation possibly introduced by either the "sandwich" method or the "quenching" method [procedure (b)] lies practically within experimental error. For the present copolymerization system, however, any systematic deviation which may be present, is believed to be more probable in the reactivity ratios resulting from the "sandwich" method rather than the "quenching" method.

The first and probably most important drawback of the "sandwich" method is that a rather high total degree of conversion hardly can be avoided, as all three stages of the experiment contribute to the conversion. High copolymer concentrations in the reaction mixture cause a slower evaporation of monomers and solvent from the reaction mixture sample, leading to a strongly increased "tailing" of the observed GLC peaks. Moreover, the limited mixing capacity of the "rocking" reactor will drastically decrease as the viscosity of the reaction mixture increases. These effects might show up as systematic errors in the calculated monomer reactivity ratios. Improvement resulting from the choice of lower monomer concentrations is limited, as in this case the relative experimental error in the observed peak areas increases. An initial total monomer concentration of 1–1.5 mole/dm<sup>3</sup> for both the "sandwich" and the "quenching" method is found to lead to the best results. Furthermore, it will be obvious that a smaller conversion during any stage of a complete experiment will invariably lead to larger experimental errors, demanding more kinetic experiments. The GLC "tailing" problems are not met to the same extent in the "quenching" method, as here only during the high-pressure stage of the experiments is the degree of conversion increasing.

TABLE I  
 Specific Reaction Conditions of the "Sandwich" Experiments of the Ethylene ( $M_1$ )-Vinyl Acetate ( $M_2$ ) Copolymerization at 600 kg/cm<sup>2</sup> and 62°C

Number of observations during the initial stage (A)	Monomer feed ratio $q_{LH}$	Number of observations during the final stage (C)	Monomer feed ratio $q_{HL}$	Degree of conversion during the high-pressure reaction, based on $M_2$ ( $f_{2HL}$ ) (%)	Total initial monomer concentration (mole/dm <sup>3</sup> )	Initiator concentration (mmole/dm <sup>3</sup> )
6	0.253	11	0.263	13.4	1.4	9.9
11	0.304	13	0.345	36.6	1.8	9.0
13	0.394	13	0.441	34.4	2.9	14.4
17	0.559	16	0.596	20.7	6.1	13.1
15	0.796	19	0.880	33.3	2.2	13.1
8	0.822	13	0.852	11.5	1.7	12.0
8	1.461	13	1.490	7.6	1.0	10.5
16	1.738	16	1.877	24.1	2.3	21.6
12	1.776	12	2.019	43.9	1.9	10.1
7	2.113	15	2.202	14.2	1.5	9.2
7	2.328	22	2.475	19.2	1.6	9.5
5	2.526	13	2.609	10.6	1.5	9.1

TABLE II  
Specific Reaction Conditions of the "Quenching" Experiments of the Ethylene ( $M_1$ )-Vinyl Acetate ( $M_2$ ) Copolymerization at 600 kg/cm<sup>2</sup> and 62°C

Number of GLC observations during initial stage (A)	Average initial monomer feed ratio	Number of observations during final stage (C)	Average final monomer feed ratio	Average degree of conversion, based on $M_2$ (%)	Total initial monomer concentration (mole/dm <sup>3</sup> )	Initiator concentration (mmole/dm <sup>3</sup> )
9	0.345	15	0.387	35.8	1.5	7.9
11	0.404	13	0.440	27.7	1.4	8.0
7	0.452	12	0.528	37.9	1.5	8.0
2	0.977	12	1.125	39.7	1.7	11.0
11	1.159	8	1.264	28.1	1.7	8.9
8	1.163	3	1.497	65.0	1.8	12.6
6	1.413	13	1.524	27.4	1.7	8.9
8	1.695	10	1.802	20.9	1.7	9.0
12	1.818	14	1.952	20.5	1.4	9.5
11	2.257	12	2.405	22.8	1.8	10.1
11	2.324	14	2.445	20.7	1.6	10.2
9	2.708	13	2.882	19.0	1.4	9.9
9	3.650	14	4.081	37.0	1.8	11.1

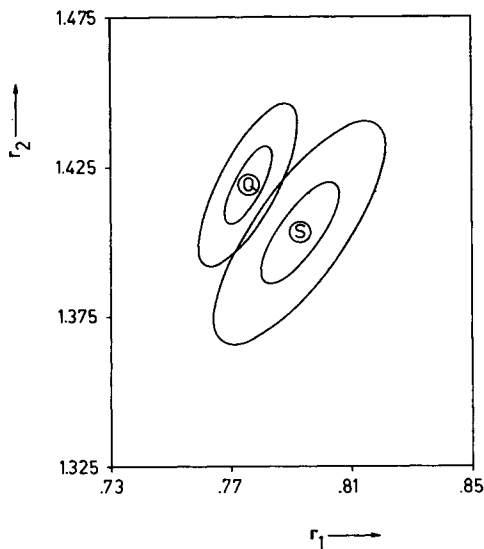


Fig. 4. Calculated confidence regions for, respectively,  $\alpha = 50\%$  and  $\alpha = 95\%$  (outermost contours), for (S) the "sandwich" experiment, and (Q) the "quenching" experiments [calculated by procedure (b)] of the ethylene ( $M_1$ )-vinyl acetate ( $M_2$ ) copolymerization at 600 kg/cm<sup>2</sup> and 62°C.

A second problem, only encountered in the "sandwich" method, is the question of the extrapolation of the monomer feed composition ( $q$ ) as a function of time in both stages A and C. Although for the present copolymerization approximation by a first-order polynomial yields a satisfactory fitting, other radical copolymerizations might follow another course and possibly require a more complicated relationship.

Another inconvenient circumstance is the difficulty of precise temperature control at the transition points from low to high pressure,  $t_{LH}$ , and from high to low pressure,  $t_{HL}$ , owing to the effects of the heats of compression and decompression. Fortunately, in the "quenching" method this problem is not met as the heats of compression and decompression assist rapid attainment of the desired reaction temperature and "quenching temperature," respectively.

As is the case in most comparisons, the "quenching" method also has some disadvantages in relation to the "sandwich" method. One drawback results from the need to include the first kinetic stage just after the induction period, where the initial pattern of monomer consumption is likely to be uncharacteristic of the reaction and may cause systematic deviations from the simple copolymer equation.<sup>9,10</sup> In certain cases, this systematic deviation was observed during low-pressure copolymerizations<sup>8</sup> where each kinetic run comprised a large number of GLC observations. It appeared that in those cases where the total degree of conversion was rather high (30–40%) these deviations had no appreciable effect on the calculated monomer reactivity ratios. The conventional procedures with their accompanying errors in copolymer analysis suffer particularly from this phenomenon, as the use of the differential copolymer equation requires the degree of conversion to be kept as low as possible, in order to maintain a nearly constant monomer feed ratio during the entire copolymerization reaction.

A simple calculation on the basis of the apparent energy of activation of the overall rate of copolymerization ( $R_p$ ) shows a decrease of  $R_p$  by a factor of 15 for

a temperature drop of 30°C in the quenching process. However, a systematic deviation due to a very slow reaction within the observed experimental error of approximately 1% still might be present.

In conclusion, the "quenching" method is considered to be the most suitable technique for the GLC determination of high-pressure monomer reactivity ratios in copolymerization. On the other hand, the "sandwich" method is also of value for high-pressure reactions when no conversion limitations are present, especially when an adequate temperature control at the transition points can be achieved. The "quenching" method may be impracticable for reactions in which the apparent energy of activation is low, but both methods are widely applicable and are particularly valuable when one of the reactants or reaction products are volatile.

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