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Effect of Pressure on Free-Radical Copolymerization Kinetics. III. An Improved Method of Measuring Monomer Reactivity Ratios under High-Pressure Conditions

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Synopsis

To investigate high-pressure copolymerizations a sampling technique has been developed enabling continual on-line GLC analysis of the reaction mixture. As a result more reliable kinetic data are obtained. This new "sequential sampling" method, allowing the use of gaseous monomers, has been tested for the copolymerization of ethylene with vinyl propionate at 118 MPa and 335 K with *tert*-butyl alcohol as solvent. The results are compared with those obtained with the "quenching" method used so far, which yields compositional data on the reaction mixture before and after the high-pressure stage, only. It is shown that the "sequential sampling" method is the most adequate method of determining high-pressure monomer reactivity ratios. Furthermore, it is an important safety feature that the present procedure can be easily remote controlled. The present experimental method is neither restricted to copolymerization nor to gas-chromatographic analysis of the reaction mixture.

INTRODUCTION

Gas/liquid-chromatographic (GLC) analysis allows a direct and accurate determination of the changing feed composition throughout a copolymerization reaction up to relatively high conversions (ca. 40%).¹⁻⁹ This experimental technique has many advantages compared to the more troublesome and inaccurate copolymer compositional analysis.¹⁰ Generally, samples are taken from the reaction mixture and injected into the gas chromatograph by means of a syringe. There are two methods permitting direct sampling from the reaction mixture by means of a specially constructed sampling device.^{5,8,9} The on-line GLC technique, described by German and Heikens,⁵ is particularly useful when gaseous monomers are involved in the copolymerization reaction. However, the use of the special disk valve¹¹ is restricted to pressures of about 4 MPa. For copolymerizations at higher pressures van der Meer and German⁸ therefore resorted to the "quenching" and the "sandwich" methods. Both methods are based on GLC analysis of the reaction mixture under low-pressure conditions just preceding and succeeding the high-pressure stage. The authors⁸ slightly prefer the "quenching" method, in which a great number of samples are taken from the noncopolymerizing reaction mixture at the two low-pressure stages. In the literature frequently a quenching like method is used, based on the laborious isolation, purification, and analysis of the copolymer formed.

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There are a number of techniques based on the continual sampling of reaction mixtures under high pressure (up to ca. 600 MPa).¹²⁻¹⁵ However, none of them can be used in case of volatile reactants or products. The aim of this article is to describe and discuss a remotely controlled on-line sampling and GLC analysis of reaction mixtures under high pressure. The merits and drawbacks of the new technique, which is referred to as the "sequential sampling" method, are compared with those of the "quenching" method. This is achieved by investigating the copolymerization of ethylene with vinyl propionate at 335 K and 118 MPa with *tert*-butyl alcohol as solvent by means of both techniques.

EXPERIMENTAL

The high-pressure apparatus is schematically shown in Figure 1 and is discussed below.

Reactor

The high-pressure reactor used in the present investigation is an Autoclave Engineers autoclave. Parts of the reactor which may come into contact with the reaction mixture are made from stainless steel A286. The maximum working pressure is 250 MPa at 350 K. A Teflon piston separates the reaction chamber from a compartment filled with the pressurizing liquid, isopropyl alcohol. This compartment is connected with the pressure control system. The reaction volume is approximately 0.75 dm³. By means of a magnetic stirrer at 500 rpm an almost ideal mixing is obtained in the reaction chamber.¹⁶ The reactor is

Fig. 1. Simplified scheme of the high-pressure apparatus used in the present investigation: (A) compartment connected with pressure control system, (B) reaction chamber, (C) internal heating coil, (D) external heating coil, (E) Teflon piston, (F) internal stirrer, (G) magnetic drive, (H) pressure control system, (K) piston pump, (L) supply flask, (M) metering valve, (N) stepping motor, (P) sample device, (Q) gas chromatograph, (R) electronic integrator, (S) recorder, (T) pneumatically actuated valve, (V) cylinder with free-moving piston, (W) piston shaft displacement transducer. Abbreviations in circles: (T) temperature, (P) pressure, (I) indicator, (C) controller.

equipped with an internal and external heating coil, through which water is circulated by means of two separate thermostats. This construction enables the desired reaction temperature to be maintained rather accurately (± 0.1 K) by adjusting the temperature of the thermostats. The reaction temperature is measured with a frequently calibrated Chromel-Alumel thermocouple.

The pressure control system is assembled from the following components: a high-pressure piston pump with remotely controllable piston stroke; a pneumatic pressure transmitter; and a pneumatically actuated valve. The pressure control system is suited for pressures up to 200 MPa.

Sampling

The special sampling disk valve (P) is described elsewhere.¹¹ The gas-chromatographic system used is the same as described previously.⁵

"Sequential Sampling" Method

The high-pressure metering valve (M in Fig. 1) (C_v value 0.08 in one turn) can be opened and closed at a controlled rate (between one turn in 7 s and one turn in 20 min). This is achieved by means of a stepping motor with adjustable speed (N). When the reaction mixture is sampled from the reactor, the pressure decreases about 1.0–1.5 MPa, but is quickly restored by the pressure control system. In the case of exclusively liquid monomers, after adequate flushing a representative sample of the reaction mixture can be easily collected and analyzed. However, this is not possible when using volatile components. In these cases the sample should be kept under pressure in order to maintain the single-phase character required for proper analysis.

Therefore, the reaction mixture is led through the sampling device (P) into a cylinder (V) against an adjustable back pressure (in our experiments 3 MPa). The total amount of reaction mixture is determined by the need of amply flushing the sampling system (ca. 5 cm³ in our experiments). In cylinder V the piston begins to move as soon as the pressure exceeds 3 MPa. This pressure is maintained by means of the pressure of the N₂ gas at the lower side of the piston. In this way, phase separation can be avoided. The quantity of reaction mixture in the cylinder is determined by means of the displacement of the piston shaft (W). As soon as sufficient reaction mixture is flushed through the sample chamber, valve M is closed and a sample of 2 μ L is injected onto the gas-chromatographic column. The mixture collected in cylinder V can be drained through valve T. In order to improve repeatability, the entire sampling cycle is automated. A rupture disk protects the sampling system against excess pressure. In this way a set of GLC observations of the copolymerizing reaction mixture at high pressure can be obtained [see Fig. 2(I)]. And from these the monomer feed ratio q and the conversion f (normally based on monomer 2) can be easily derived.^{5,8}

"Quenching" Method

In this method three different stages have to be distinguished, as schematically shown in Figure 2(II). During the first stage (A) the pressure is 3.4 MPa and the temperature is approximately 320 K. Under these conditions no reaction

Fig. 2. Plots of the monomer feed ratio q versus both the reaction time and the degree of conversion based on monomer 2, f_2 , for a sequential sampling experiment (I) and a quenching experiment (II).

occurs and a set of GLC observations is made. In stage B at the desired pressure and temperature the copolymerization is allowed to continue during a fixed period of time. The reaction is quenched by a quick drop of pressure and temperature. Finally, during stage C a second set of GLC observations is made from the noncopolymerizing reaction mixture. In this way the monomer feed composition before and after the high-pressure stage is determined very accurately.

Copolymerization

The copolymerization of ethylene (Eth) with vinyl propionate (VP) in *tert*-butyl alcohol (TBA) with α, α' -azobisisobutyronitrile (AIBN) as free-radical initiator has been carried out with both the sequential sampling and the quenching techniques. The purification and physical properties of the reagents are given elsewhere.¹⁷ The gas-chromatographic conditions were column length 2 m; column temperature 325 K; stationary phase 15% by wt of a mixture of 30% by wt of diglycerol and 70% by wt of quadrol on chromosorb P-AW 60–80 mesh; sample size 2 μ L. The details of the experiments are given in Tables I and II. The monomer reactivity ratios have been evaluated by means of the VLG method.¹⁰ This procedure, based on the integrated copolymer equation, considers experimental errors in *both* measured variables. In addition, the r values are compared with those obtained with the recently developed WLS method.¹⁸

RESULTS AND DISCUSSION

The r values calculated for the Eth-VP copolymerization at 118 MPa and 335 K with the sequential sampling and the quenching methods are given in Table III. The 95% confidence regions for the r values obtained by means of the VLG procedure are shown in Figure 3. The r values calculated by means of the WLS procedure are not solely added to emphasize the power of this very simple method but also for reasons of comparison of the results of both methods. The mathe-

TABLE I
Experimental Conditions of the Copolymerization of Ethylene (M_1) with Vinyl Propionate (M_2) at 118 MPa and 335 K with *tert*-Butyl Alcohol as Solvent by Means of the "Quenching" Method

Number of GLC observations during the initial stage	Average initial monomer feed ratio	Number of GLC observations during the final stage	Average final monomer feed ratio	Average degree of conversion, based on M_2 (%)	Total initial monomer concentration (mol/dm ³)	Initiator concentration (mmol/dm ³)
8	3.330	11	3.526	17.1	1.3	6.1
13	2.813	10	2.926	12.6	1.3	5.1
12	2.582	10	2.701	14.3	1.3	6.1
13	2.224	9	2.319	13.6	1.3	5.1
13	1.480	14	1.637	30.5	1.4	6.1
12	1.470	11	1.556	18.6	1.3	5.1
12	1.138	12	1.196	16.6	1.5	6.2
12	1.116	10	1.183	19.3	1.1	5.6
10	1.035	11	1.189	40.3	1.3	5.6
9	0.844	11	0.896	20.2	2.1	5.1
12	0.754	13	0.825	29.2	1.4	5.6
12	0.742	14	0.817	31.1	2.0	5.1
11	0.528	11	0.570	26.6	1.5	5.1

TABLE II
Experimental Conditions of the Copolymerization of Ethylene (M_1) with Vinyl Propionate (M_2) at 118 MPa and 335 K with *tert*-Butyl Alcohol as Solvent by Means of the "Sequential Sampling" Method

Initial monomer feed ratio q_0	Final monomer feed ratio	Conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mol/dm ³)	Initiator concentration (mmol/dm ³)
3.896	4.069	14.1	12	1.5	3.7
3.000	3.169	17.7	15	1.8	4.2
2.816	3.037	23.7	21	1.7	2.7
2.760	2.989	24.8	18	1.4	3.3
2.336	2.464	17.6	12	1.5	3.3
1.819	2.000	29.7	21	1.3	2.8
1.348	1.455	25.2	19	1.1	5.6
1.342	2.475	30.1	20	1.4	2.8
1.081	1.179	28.5	13	1.6	4.7
1.022	1.116	30.0	12	1.9	3.7
0.940	1.018	27.0	11	1.8	3.7
0.939	1.013	26.3	14	1.8	4.2
0.936	1.021	29.1	11	1.8	4.7
0.581	0.631	28.8	9	0.9	3.3
0.565	0.618	31.3	12	1.4	2.7
0.555	0.604	29.3	14	1.4	2.7
0.482	0.531	33.5	13	1.6	2.8

TABLE III
Monomer Reactivity Ratios for the Ethylene (M_1)-Vinyl Propionate (M_2) Copolymerization at 118 MPa and 335 K with the "Sequential Sampling" and "Quenching" Methods Calculated by means of the VLG Procedure and the WLS Procedure

Calculation procedure		"Sequential Sampling" method	"Quenching" method
VLG	r_1	0.69 ± 0.02^a	0.67 ± 0.01^a
	r_2	1.27 ± 0.03	1.28 ± 0.02
WLS	r_1	0.68 ± 0.02	0.68 ± 0.02
	r_2	1.26 ± 0.03	1.30 ± 0.03

^a Approximate standard deviations.

mathematical framework of the WLS method is basically different from that of the VLG method. Therefore, the agreement of the corresponding r values for both calculation procedures corroborates the validity of the Alfrey-Mayo scheme^{19,20} to describe the copolymerization of Eth with VP for both experimental methods. In addition an objective mathematical F test,²¹ based on the statistical comparison of residual sums of squares, can be used, with which it is possible to check the goodness of fit of any copolymerization scheme. In this model fitting test the calculated $F_{r_2}^{r_1}$ is compared with the critical value $F_{r_2}^{r_1}(\alpha)$. A large value of $F_{r_2}^{r_1}$ leads to the conclusion that the particular scheme is not appropriate to describe the observed kinetic behavior. However, in applying the F test to the present Eth-VP copolymerization there is a contradiction between the two experimental methods. In case of the sequential sampling method the F test justifies application of the Alfrey-Mayo scheme [$F_{213}^{15} = 0.70 < F_{213}^{15}(0.05) = 1.67$], whereas in the quenching method the F test [$F_{270}^{11} = 3.84 > F_{270}^{11}(0.05) = 1.79$] leads to rejection of the Alfrey-Mayo scheme. This is also found in other copolymerizations investigated by means of the quenching method.²² Furthermore, in the case of the VLG method the standard deviations, and with them the cal-

Fig. 3. Calculated confidence region ($\alpha = 95\%$) for the copolymerization of ethylene (M_1) with vinyl propionate (M_2) at 118 MPa and 335 K with *tert*-butyl alcohol as solvent by means of the sequential sampling method (S) and the quenching method (Q).

culated confidence regions (see Fig. 3), are greater in the sequential sampling method than in the quenching method. Both discrepancies are due to the different design of the experiments. In the sequential sampling method the observations are distributed along the entire curve, whereas in the quenching method the observations are located at the extremities of the line. Mathematically it can be easily shown that the precisions of the quenching and the sequential sampling methods are in the proportion of approximately 3 to 5 (see the Appendix for a typical example). However, in the quenching method the induction period and the first kinetic stage thereafter are included, where the pattern of monomer consumption will be uncharacteristic of the copolymerization. This may cause systematic deviation from a scheme based on the steady-state assumption such as the Alfrey-Mayo scheme.^{8,23} This explains the inability of the Alfrey-Mayo scheme to describe the quenching experiments by the results of the F test. In case of the sequential sampling method this stage can be omitted.

Further proof was obtained by simulating copolymerization data in the following way.²⁴ For a number of selected r values ten copolymerization experiments were simulated with initial monomer feed ratios that varied from 0.4 with steps of 0.4 to 4.0 and M_2 conversion of 25%. In addition, the number of observations per experiment was varied. In the case of the quenching method the number of observations were equally distributed among the two low-pressure stages. For each experiment the M_2 conversion was increased from zero by equal amounts (depending on the number of observations) and the corresponding monomer feed ratio was computed from the integrated Alfrey-Mayo equation. Ideal GLC areas (without measurement errors) were computed and those areas were disturbed by a normal error. The standard deviations of the areas of the two monomers and the solvent were chosen as 0.5, 0.5, and 0.75%, respectively. The areas thus obtained were then used to recalculate the monomer feed ratio q and the M_2 conversion f_2 . The resulting data were then analyzed by the VLG method. The results are given in Table IV.

Primarily, it can be seen from this table that the precision of both techniques improves as the number of observations increases. Secondly, the precisions of the sequential sampling method and the quenching method are in the proportion of 5 to 3. Thirdly, the simulated quenching experiments are described by the Alfrey-Mayo scheme. This leads to the important conclusion that the deviation from the Alfrey-Mayo scheme found in the real quenching experiments originates from the experimental technique. As a consequence it seems justified to state that the results of many investigations which are based on the quenching like procedure of copolymer compositional analysis are less well founded than the authors have claimed.

There are more reasons that support the sequential sampling method. The quenching method is based on analysis of the *nonreacting* mixture at a low temperature prior to and after the reaction stage. Therefore it cannot be used for reactions with a low energy of activation. It is obvious that the sequential sampling method bears no such limitations. It allows one to impose immediately the desired pressure and temperature and to start the sampling sequence. Moreover the sequential sampling method gives a considerable gain in time.

TABLE IV
Effect of Experimental Technique and Number of Observations on Copolymerization Parameter Estimates Calculated with the VLG Procedure

Copolymerization parameters		Number of observations	"Sequential sampling" method			"Quenching" method		
r_1	r_2		r_1	r_2	F_2^{VI}	r_1	r_2	F_2^{VI}
0.2	0.5	140	0.204 ± 0.009	0.488 ± 0.016	0.63	0.199 ± 0.006	0.497 ± 0.010	0.48
		260	0.191 ± 0.007	0.483 ± 0.012	0.60	0.198 ± 0.004	0.496 ± 0.007	0.94
		400	0.211 ± 0.006	0.516 ± 0.010	0.91	0.205 ± 0.004	0.510 ± 0.006	1.03
0.5	2.0	140	0.518 ± 0.020	2.127 ± 0.082	0.53	0.502 ± 0.012	2.035 ± 0.048	0.63
		260	0.494 ± 0.015	2.055 ± 0.062	0.73	0.495 ± 0.009	2.019 ± 0.036	0.95
		400	0.493 ± 0.012	2.013 ± 0.048	1.23	0.502 ± 0.007	2.028 ± 0.029	0.82
4.0	0.5	140	3.896 ± 0.064	0.459 ± 0.020	0.23	3.962 ± 0.041	0.477 ± 0.013	0.41
		260	4.046 ± 0.050	0.510 ± 0.015	0.69	4.013 ± 0.030	0.501 ± 0.009	0.70
		400	3.924 ± 0.039	0.480 ± 0.012	0.43	3.954 ± 0.024	0.489 ± 0.007	0.87

^a In the case of 140 observations $F_2^{VI}(0.05) = 2.02$ otherwise $F_2^{VI}(0.05) = 1.94$.

CONCLUSIONS

The quenching method (and with that quenching like methods based on copolymer compositional analysis) is questionable in discriminating among different copolymerization schemes describing the proposed kinetics. On the other hand, a number of reasons supports the adequacy of the sequential sampling method described in this article. In addition, the technique is not restricted to copolymerization or to GLC but is widely applicable in combination with various other analytical techniques. The technique is particularly suitable in case of volatile reactants or products.

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APPENDIX

A Simple Example to Illustrate the Effect of Design Choice on the Variance of the Parameter Estimate

Let the observational model be

$$y_i = \beta x_i + \text{error}$$

where x_i is known, $0 \leq x_i \leq 1$, and $i = 1, \dots, 10$. We also assume that $\text{var}_i = \sigma^2$. The least-squares estimate for β is given by $\sum x_i y_i / \sum x_i^2$, with variance equal to $\sigma^2 / \sum x_i^2$. In a quenching like design we would choose $x_i = 1$ for all i , whereas in a sequential-sampling-like experiment our choice would be $x_i = 1/10$. The corresponding standard deviations of the parameter estimate are in a proportion of 3 to 5. This ratio is not very dependent on sample size. Although not congruent to our actual experimental situation, this example may nevertheless serve as a first approximation. Consequently, we expect the ratio of the computed standard deviations of the quenching and sequential sampling estimates to be equal to about $3/5$. This is confirmed by the numbers in Table IV.

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