The Copolymerization of Vinyl Chloride with 1-Olefins. I. A New Method of Investigation of the Kinetics of Homopolymerization and Copolymerization of Vinyl Chloride

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Synopsis

The indirect volumetric method following the amount of monomers in the heterogeneous liquid reaction mixture in a constant volume of samples periodically withdrawn by means of gas chromatography. This new method utilizes periodic sampling of the heterogeneous reaction mixture from the reactor during the reaction and gas chromatographic determination of the unreacted monomers contained in the sample. Its suitability and reliability were verified for the suspension homopolymerization of vinyl chloride. The reproducibility of sampling and the accuracy of determination of the degree of conversion and of the initial reaction rate were investigated. The conversion curves obtained by this method are compared with those obtained by the classical gravimetric method.

INTRODUCTION

The limited choice of methods available for the study of the heterogeneous polymerizations or copolymerizations vinyl chloride stimulated work which led to the development of a general method based on periodic sampling of the heterogeneous mixture of condensed phases (immiscible liquids, solid polymer), followed by the gas chromatographic determination of the monomer or monomers in the aliquot so obtained.

The major problem which arose was sampling of the heterogeneous reaction mixture. The difficulty of sampling and of a quantitative analysis of the sample is due to the heterogeneity of the reaction medium, the variation in morphology of the polymer particles formed, and the fact that the system is under pressure. Sampling must not affect the relative amounts of the individual components, and hence the course of the polymerization. This is a complicating factor, especially when small-size laboratory reactors are used. This is why the amount of the monomers and not of the final product was examined in the samples.

A piston sampling valve[1] (Fig. 1) placed in the outlet at the bottom of the reactor was employed to sample the heterogeneous reaction mixture during the suspension polymerization of vinyl chloride. Through a cylindrical slot in the piston of the valve, a sample of constant volume (ca. 50 μL) was taken periodically directly from the reactor.

All chromatographic operations, including the control of the piston sampling valve, and other operations were programmed in 1-h cycles. This program was controlled by the microprocessor of the gas chromatograph.

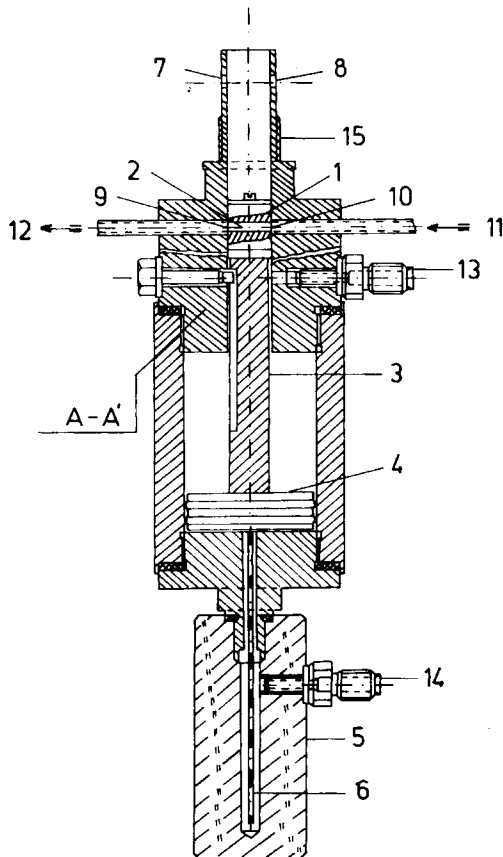* Present address: ORGREZ, 170 00 Prague, Czechoslovakia.

Fig. 1. Cross section of the piston sampling valve. (1) sampling piston; (2) sampling slot; (3) pull rod of the piston; (4) control piston; (5) transparent cylinder; (6) control rod; (7, 8) sampling openings in the jacket of the sampling piston; (9, 10) sampling openings in the jacket of the sampling piston; (11, 12) inlet and outlet of the carrier gas; (13, 14) outlets for pneumatic control; (15) thread for the opening in the bottom of the reactor (cross section A—A' has been turned through an angle of 90°).

EXPERIMENTAL

Materials

Vinyl chloride (Czechoslovakian made), impurities content 90 ppm at most (216 g), dicetylperoxydicarbonate (Kema-Nord, Stockholm), peroxides content 73.5%, active oxygen content 2.2% (0.20035 g), hydroxypropylmethylcellulose (Dow Chemical Co.), viscosity of a 2% solution 4.598×10^{-2} Pa·s (13.12 g), and distilled water (515 g). The values given in parentheses are mass amounts of the individual components of the reaction mixture used in the homopolymerizations of vinyl chloride performed at $55 \pm 0.1°C$ for 8 hr at a stirrer speed of 500 rpm.

Experimental Arrangement

The equipment used consisted of a stainless steel reactor, with a jacket, 1 dm^3 in volume (Ingenieurbureau, SFS, Zürich), water thermostat, electronic measurement, and temperature control system for the reactor (Knauer, West Berlin), a temperature and pressure recording system for the reactor, a gas chromatograph (Hewlett-Packard, Model 5834 A), and a new device for automatic sampling of the heterogeneous reaction mixture in the reactor and the quantitative transfer of unreacted vaporized monomers into the chromatograph.

Figure 2 gives a schematic view of the experimental layout. The sampling slot containing the sample of the heterogeneous reaction mixture is transferred pneumatically into the carrier gas line of the chromatograph. Additional carrier gas led through a solenoid valve (13) transfers the sample quantitatively into a heated stainless steel desorber (80°C), where the monomers are quickly desorbed from the polymer and the water is vaporized. Water vapors condense in the stainless steel air cooler, and water is collected in the separator. Simultaneously with, or within a short time (6 s) after the operation of the piston sampling valve mentioned above, a four-way valve (6) is operated so as to connect the sampling system to the carrier gas line of the gas chromatograph. The gaseous monomers are thus transferred into the fractionation column of the gas chromatograph. In order to prevent the transfer of the pressure surge to the circuit of the carrier gas, the latter is led to the piston sampling valve through a special stainless steel capillary resistance (14); an identical capillary was also installed in the carrier gas line upstream of the fractionation column (7).

By using a synchronized operation of the solenoid valve (10), the six-way valve
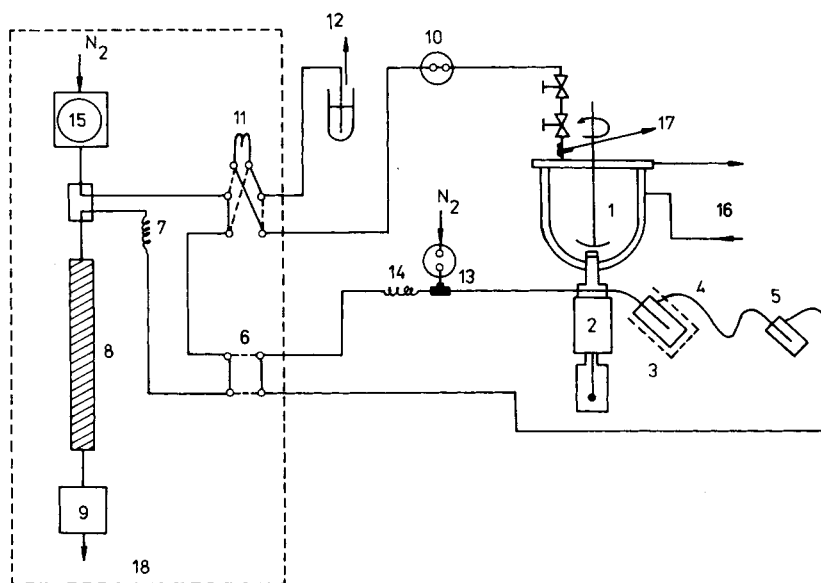

Fig. 2. Schematic view of sampling by means of piston sampling valve: (1) polymerization reactor; (2) piston sampling valve; (3) thermal desorber; (4) air cooler; (5) separator of condensed water; (6) four-way valve; (7) flow restrictor; (8) chromatographic column; (9) FID; (10) solenoid valve; (11) six-way valve; (12) hydraulic seal; (13) solenoid valve; (14) flow restrictor; (15) injection port; (16) thermostated bath; (17) pressure measurement; (18) gas chromatograph (Hewlett Packard 5834 A).

(11) and the four-way valve (6), a constant volume of the sample taken from the gas space of the reactor can also be analyzed.

Program of the Gas Chromatograph

Isothermal chromatographic fractionation of the components (50°C) proceeded on a column, 2.5 mm in diameter, 12 m long, packed with 20% by weight β,β'-oxydipropionitrile[2] on Chromaton N-AW, particle size 0.250–0.315 mm.

A flame-ionization detector (150°C) was used with nitrogen as the carrier gas (30 cm³/min).

The time program for automatic sampling of the gas phase and of the heterogeneous reaction mixture was chosen so that the periodic cycle of analyses included two samplings of the heterogeneous reaction mixture with one sampling of the gas phase between them. The whole procedure including the printout of values took 60 min.

RESULTS

Nonpolymerization Runs

In order to examine sampling reproducibility, nonpolymerization runs were used. The experiments were arranged so that suspension stabilizers, water, and vinyl chloride were dosed into the reactor without initiators in the same amounts as in the polymerization. Under the reaction conditions prescribed for polymerization (55°C), sampling of the equilibrium gas and heterogeneous liquid phase was controlled by the program. The results of the response of the flame-ionization detector (AREA) to the sample size and maximal relative errors in the sampling calculated from the results are summarized in Table I.

Experimental Verification of Performance of Sampling Apparatus in Suspension Homopolymerization of VC

The experimental arrangement designed for the investigation of the polymerization and copolymerization of vinyl chloride was tested by a number of

TABLE I
Verification of Reproducibility of Sampling of Gas and Heterogeneous Phases[a]

Sampling no.	Stirrer (rpm)	Gas phase [(AREA) $\times 10^5$]	A[a]	Liquid phase [(AREA) $\times 10^6$]	A[a]
1	300	3859		3173	
2	300	3860	−1.1	3175	−0.9
3	300	3803	+0.4	3201	+2.6
4	300	3848		3285	
5	300	3858		3181	
6	600	3865		3222	
7	600	3862		3246	
8	600	3879	±0.3	3255	±0.8
9	600	3879		3221	
10	600	3857		3202	

[a] Maximum relative error (%).

homopolymerizations.   Its long-term operational reliability and the accuracy of determination of the degree of conversion and of the initial reaction rate by employing the above method were examined.   The conversion curves obtained by this method were compared with those provided by the classical gravimetric method.

For representative sampling of the heterogeneous reaction mixture, the samples taken from the reactor had to be at least tens of microliters in volume. As a consequence, however, the amount of the analyzed gas components became so high that a linear relation between concentration and the detector's response no longer held.   For this reason, calibration had to be carried out by dosing various volumes of vinyl chloride (gas-tight Hamilton syringe) directly into the injection port.   The dosed volume of the component was recalculated to absolute mass concentrations.   At least five repeated analyses were run to calculate the average area of the peak corresponding to the given concentration.   The relative error in the peak areas for the same injected volume of vinyl chloride did not exceed 3% rel.   From these data a calibration curve was constructed.

Figure 3 shows a chromatographic record taken in the 4th h of the suspension polymerization of vinyl chloride.   Using the calibration graph, the peak areas in the chromatograms were converted into mass equivalents, corresponding to the amount of the monomer in the aliquot.   The same values plotted as a function

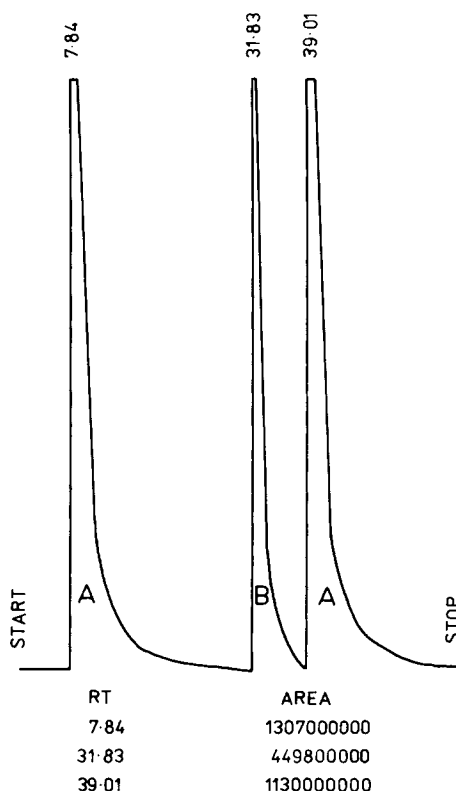| RT	AREA
7·84	1307000000
31·83	449800000
39·01	1130000000

Fig. 3. Chromatogram of the heterogeneous reaction mixture and gas phase recorded in 4th hour of the homopolymerization of vinyl chloride: (A) sample of heterogeneous condensed phases; (B) sample of vapor phase.

of time gave information on the rate of the loss of the monomer in the reaction mixture during the polymerization.

The time dependence of the chromatographically obtained mass amounts of vinyl chloride (G) in the samples and of the conversions of the monomer (C) calculated from these values is shown in Figure 4.

The reproducibility and reliability of the conversion curves obtained by the described method was evaluated statistically. Table II presents the chromatographically determined amounts of unreacted vinyl chloride in samples taken
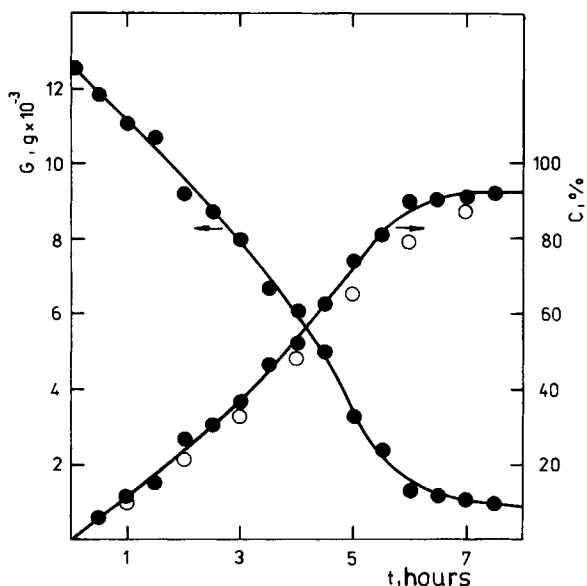

Fig. 4. Reaction course of the homopolymerization of vinyl chloride investigated chromatographically (●) and gravimetrically (○).

TABLE II
VCM (mg) in Sampler as Function of Time

Time (min)	Polymerization run no.				
	1	2	3	4	5
0	15.0	13.0	12.6	12.3	11.4
30	14.2	11.5	11.9	11.6	11.2
60	12.6	10.6	11.1	11.5	9.4
90	12.4	10.9	10.7	9.5	9.3
120	11.4	9.5	9.2	9.4	8.1
150	10.4	8.6	8.7	8.2	7.5
180	8.9	7.8	8.0	7.3	6.5
210	7.9	7.0	6.7	6.5	5.9
240	6.4	5.7	6.1	5.9	4.8
270	4.8	4.8	5.0	4.6	3.8
300	3.1	3.5	3.3	3.8	2.8
330	2.0	2.5	2.4	2.8	1.8
360	1.5	1.8	1.3	2.2	1.9
390	1.3	1.3	1.2	1.6	1.2
420	1.1	1.2	1.1	1.0	0.8
450	1.0	1.1	1.0	1.1	0.6
480	0.9	1.0	1.0	1.2	0.8

TABLE III
Conversion of Vinyl Chloride, C, as Function of Time

Time (min)	Polymerization run no.				
	1	2	3	4	5
0	0	0	0	0	0
30	5.3	8.7	5.6	5.7	1.8
60	16.0	15.9	11.9	6.5	17.5
90	17.3	13.5	15.1	22.8	18.4
120	24.0	24.6	27.0	23.6	28.9
150	30.7	31.7	31.0	33.3	34.2
180	40.7	38.1	36.5	40.6	43.0
210	47.3	44.4	46.8	47.2	48.2
240	57.3	54.8	51.6	52.0	57.9
270	68.0	61.9	62.7	62.6	66.7
300	79.3	72.2	73.8	69.1	75.4
330	86.7	80.2	81.0	77.2	84.2
360	90.0	85.7	89.7	82.1	83.3
390	91.3	89.7	90.5	87.0	89.5
420	92.7	90.5	91.3	91.9	93.0
450	93.3	91.3	92.1	91.0	94.7
480	94.0	92.1	92.1	90.2	93.0

periodically from the heterogeneous reaction mixture in five homopolymerizations. From these the conversion of vinyl chloride was calculated (Table III). The assembly of conversion data not affected by the magnitude of the sampling slot used were treated statistically.

The accuracy of determination of conversion was estimated by applying the t-test[3] based on the Student distribution function. The tabulated value found for a 95% confidence that the measured value does not go beyond the determined reliability boundaries and for the number of the degrees of freedom $n = N - 1$ = 4 was $t = 2.78$.

The results of the statistical treatment (Table IV) show that, for the whole experimental range, the accuracy of determination of conversion may be expressed approximately by

$$C_i = \overline{C} \pm 3.0(\%) \tag{1}$$

The accuracy of the individual conversion determinations in the course of homopolymerizations is shown in Figure 5.

The conversions obtained by this method were compared with those of the classical gravimetric method. The curve was constructed by using seven data points, obtained by interrupting the reaction at the various periods. For each individual run the product was isolated, dried, and weighed.

Unlike the gravimetric method, only monomers contained in the heterogeneous reaction mixture are mass-balanced in the calculation of conversion by our method. For this reason, gravimetric results are always lower. In order to obtain a more accurate comparison between the two methods, the gravimetric results were therefore corrected with respect to the amount of the monomer present in the gas phase at the given degree of conversion (effect of volume contraction of the reaction mixture, or changes in pressure). As a result of the volume contraction of the reaction mixture, concentration changes also take place in the

Time (min)	$\bar{x}$ (%)	s (%)	$\pm t \cdot s / N$ (%)
0	0	0	0
30	5.42	2.45	3.04
60	13.56	2.76	3.42
90	17.42	3.56	4.41
120	25.62	2.25	2.80
150	32.18	1.51	1.87
180	39.78	2.52	3.12
210	46.78	1.42	1.76
240	54.72	2.91	3.61
270	64.38	2.77	3.43
300	73.96	3.79	4.70
330	81.86	3.68	4.56
360	86.16	3.61	4.48
390	89.60	1.62	2.01
420	91.88	1.02	1.26
450	92.48	1.53	1.90
480	92.28	1.40	1.74

samples—the relative participation of the aqueous phase in the samples increases with time. The effect of this phenomenon on the exactness of determination of the degree of conversion can, however, be neglected. The amount of vinyl chloride in the gas phase in the reactor under given experimental conditions at
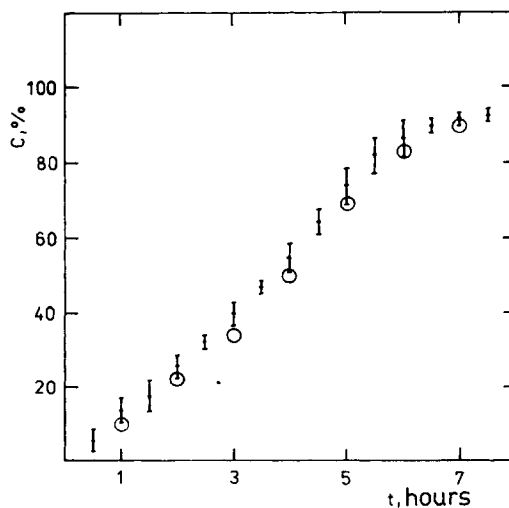

Fig. 5. Accuracy of the chromatographic determination of conversion during the homopolymerization of vinyl chloride; comparison with results obtained by the gravimetric method (O).

TABLE V
Correction of Gravimetric Data[a]

C_{GC}	C_w	VCM[b] (g)	$C_{w\ adj}$	$C_{GC} - C_{w\ adj}$
0	0	8.11	—	—
13.6	9.6	8.38	10.0	3.6
25.6	21.2	8.85	22.2	3.4
39.8	33.0	9.28	34.5	5.3
54.7	48.2	9.89	50.5	4.2
74.0	65.5	10.88	69.0	5.0
86.2	79.0	11.32	83.3	2.9
91.9	87.1	7.12	90.1	1.8

[a] Conversion (%): C_{GC} chromatographic, C_w gravimetric, $C_{w\ adj}$ gravimetric adjusted.
[b] Amount of monomer in the gas phase.

various degrees of conversion and its effect upon the correction of gravimetric data can be seen in Table V. The simple relationship

$$C_{w\ adj} = \left(\frac{PVC}{VCM - VCM^g}\right) \times 100 \qquad (2)$$

was used as adjust experimental data, where PVC is the amount of polymer formed, VCM is the amount of monomer dosed into reactor, and VCM^g is the amount of monomer in gaseous phase. Gravimetric and adjusted gravimetric conversion are plotted in Figures 4 and 5, respectively.

Using this indirect volumetric method, it is possible to determine the amount of monomers in the reaction mixture, which in turn allows us to calculate the initial reaction rates. For the homopolymerizations of vinyl chloride 1–5, the value obtained was determined with an accuracy of 9.5 ($\pm$0.8) $\times$ 10^{-5} mol/ dm^3·s.

DISCUSSION

In nonpolymerization runs good reproducibility of sampling of the heterogeneous liquid and equilibrium gas phase of the reactor was achieved. The results obtained indicate that the scatter is lower at the higher of the two stirring rates.

A long-term operation involving a considerable number of polymerizations of vinyl chloride allowed us to check the operational reliability of the apparatus. It was demonstrated that, by employing the described procedure, a representative sample of the reaction mixture could be collected from the reactor and the amount of monomers contained therein could be examined irrespective of the degree of conversion attained.

Statistical treatment of the collected results of the polymerizations of vinyl chloride carried out under the same conditions has demonstrated reasonable accuracy of determination of the degree of conversion throughout the whole experimental range [eq. (1)].

Plotting the results of the statistical treatment (Fig. 5) shows that the greatest relative error appears in the determinations of conversion in the range of the lowest and highest reaction rates, or in the initial stage and in the region of a steep rise in the polymerization rate ("hot spot").[4] It ought to be borne in mind that factors affecting the polymerization also participate in the scatter of data such as, e.g., homogeneity of the initiator, quantitative transfer of the reaction com-

ponents into the reactor, and dosage of the monomer. The scatter of the gas-chromatographic results is probably caused by fluctuation of the growing polymer particles and by nonuniform dispersal of the monomer in the sampling slot of the piston valve.

Comparison of the conversion curve obtained by the indirect volumetric method with that of the gravimetric method demonstrated that even the uncorrected data produce a similar shape of curve throughout the whole conversion range (Fig. 4). Very good agreement between the curves was obtained with appropriate correction of the amount of vinyl chloride in the gas phase (Fig. 5). The differences between the two determinations during the reaction are on the average 3.7%. This conclusion is based on the assumption that the gravimetric method is exactly quantitative.

Chromatographic analysis also make possible a reliable determination of polymerization rates. Analyses of samples taken from the gas phase have no kinetic importance in the homopolymerization of vinyl chloride: Their purpose was to test the sampling technique. Sampling the vapor phase would be of use only when most then one monomer is involved, such as, for example, in the copolymerizations of vinyl chloride with 1-olefins.

CONCLUSIONS

For the investigation of the kinetic course of the suspension polymerization of vinyl chloride, a general method has been proposed, based on a periodic volumetric sampling of the condensed phases of the heterogeneous reaction mixture during the reaction and on the gas chromatographic determination of the amount of unreacted monomers in the aliquot so obtained.

The procedure for sampling the heterogeneous reaction mixture directly from the reactor utilizes an automatically controlled piston sampling valve designed and constructed in these laboratories. Fully automated operation of the apparatus was provided by coupling with a gas chromatograph, which in addition to the usual chromatographic operations also operates peripheral devices according to specified program. Good reproducibility of the sampling, satisfactory accuracy of the determination of the degree of conversion, and good agreement between results obtained by the suggested method and values determined by the classical gravimetric method were obtained.

By using the new method, it is possible in a single polymerization run to determine the conversion curve of vinyl chloride as well as the reaction rate in various stages of the polymerization. One is justified in assuming that this method, which has been demonstrated successfully for the suspension polymerization of vinyl chloride, may be extended to copolymerization as well as to emulsion and solution systems.

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