

# The Copolymerization of Vinyl Chloride with 1-Olefins. II. An Investigation of the Copolymerization Reaction of Vinyl Chloride and Propene

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## Synopsis

The conversion curve of the copolymerization of vinyl chloride with propene and the conversion curves of both monomers were determined, their initial reaction rates compared, and the copolymerization parameters determined by a method which utilizes periodical sampling of a heterogeneous reaction mixture from the reactor during the reaction and gas-chromatographic determination of unreacted monomers contained in the sample. The agreement between the final conversion values determined chromatographically and gravimetrically was evaluated by using results of a series of copolymerizations of vinyl chloride containing various amounts of propene in the initial monomeric mixture (5–30 wt %) carried out under the same conditions.

## INTRODUCTION

In our earlier paper,<sup>1</sup> a new method was described which had been worked out for the investigation of the polymerization and copolymerization reactions of vinyl chloride.

In this study the method was used in an investigation of the copolymerization of vinyl chloride containing various amounts of propene in the initial monomeric mixture (5,10,15,20,25,30 mass %) carried out under the same conditions. The final conversion values of these copolymerizations determined by employing this method and the gravimetric method were compared. The analysis of differences between the two determinations has as its objective an estimation of the suitability of the new method not only for the homopolymerizations, but also for the copolymerizations of vinyl chloride.

By using the time dependences of the chromatographically determined amount of monomers in the sample, the initial reaction rates of both monomers were calculated for the given composition of the initial monomeric mixture, and their conversion curves were derived. The results of the chromatographic analyses were also employed in the determination of the respective copolymerization parameters.

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## EXPERIMENTAL

### Materials

Chemicals listed below in amounts indicated in brackets were used in the polymerizations.

Vinyl chloride (Spolana, Neratovice, 205.2–151.2 g), impurities content 90 ppm at most (H<sub>2</sub>O 73 ppm, methyl chloride 9 ppm, vinylacetylene 6.5 ppm, 1,3-butadiene 5 ppm, ethyl chloride 4 ppm, iron <0.5 ppm).

Propene (Slovnaft, Bratislava, 10.8–64.8 g), impurities content 0.7% at most (hydrogen 1290 ppm, alkanes C<sub>1</sub>–C<sub>4</sub> 0.5%).

Dicetylperoxydicarbonate (Kema-Nord, Stockholm, 0.80140 g), peroxides content 73.5%, active oxygen content 2.2%.

Hydroxypropylmethylcellulose (Dow Chemical Co., 13.12 g; 3.8% solution), viscosity of 2% solution  $4.598 \times 10^{-2}$  Pa·s.

Distilled water (515 g).

### Experimental Techniques

The experimental techniques used have been described earlier.<sup>1</sup> Isothermal chromatographic separation of gasified monomers from the sample was carried out on a column 2.5 mm in diameter, 12 m long, packed with 20% mass of  $\beta,\beta$ -oxydipropionitrile<sup>2</sup> on Chromaton N-AW, grain size 0.250–0.315 mm. A flame-ionization detector was used in the detection, with nitrogen as the carrier gas. The time program for automatic sampling of the gas phase and of the heterogeneous reaction mixture was adjusted so that the periodic cycle of analyses included four samplings from the heterogeneous reaction mixture followed by one sampling from the gas phase. The whole program including the printout took 60 min.

Vinyl chloride was copolymerized with various amounts of propene under the same reaction conditions, using a uniform working instruction. The instruction was chosen so as to contain the lowest possible number of components, thus ruling out the possible effect of some admixtures on the kinetic course of the copolymerization reaction. Even under such conditions, however, a sufficiently stable suspension was obtained during the copolymerization within the whole concentration range (5–30 mass % of 1-olefin in the initial monomeric mixture), and homogeneous products without agglomerates were obtained. The values given in brackets (cf. Materials) are the weight amounts of the individual components of the reaction mixture used in copolymerizations carried out at  $55 \pm 0.1^\circ\text{C}$  for 18 h at stirrer revolutions  $500 \text{ min}^{-1}$ .

The copolymers thus obtained were decanted each time with 2 dm<sup>3</sup> of distilled water and washed with ca. 1 dm<sup>3</sup> of distilled water on an S 1 glass filter. Samples dried to constant mass at 60°C were weighed and sifted on a sieve 0.250 mm, or on sieves 0.063 mm and 0.315 mm, if necessary. The propene content in the copolymer was calculated from the determination of carbon by elemental analysis on a C—H—N automatic analyzer (Perkin-Elmer, Model 240) and from the chlorine determination by the modified<sup>3</sup> Schöniger method.<sup>4</sup> The intrinsic viscosities were measured by employing the standard dilution method in tetrahydrofuran.

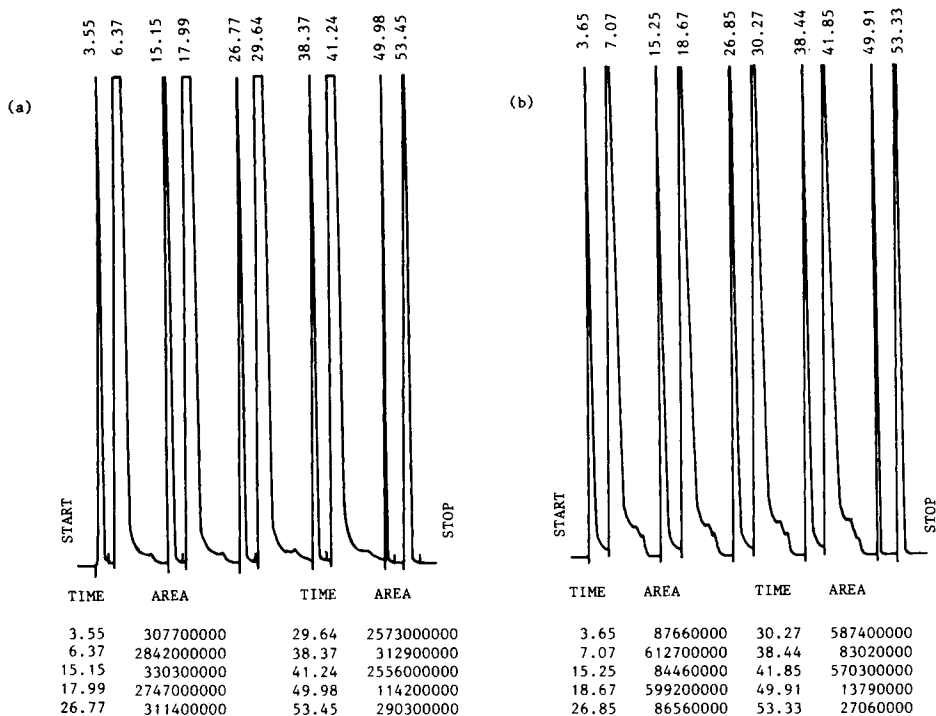


Fig. 1. Chromatogram of an analysis of the heterogeneous reaction mixture and gas phase taken in (a) 1st and (b) 6th h of the copolymerization of vinyl chloride with 10.4 mass % of propene in the initial monomeric mixture.

## RESULTS

Figure 1 shows examples of chromatographic records made at the beginning and after 6 h of the copolymerization of vinyl chloride with 10.4 mass % of propene in the initial monomeric mixture. By using the respective calibration plots (Fig. 2), the areas shown in the chromatograms (AREA) were transformed into mass equivalents corresponding to the analyzed amounts of monomers in the samples.<sup>1</sup>

The time dependence of chromatographically obtained mass quantities of the particular monomers in the samples and the conversion curves derived therefrom are shown in Figures 3–8. The total conversion curves of copolymerization may be obtained in a similar way. The total conversion curves of the copolymerizations of vinyl chloride with 5.3 and 20.2 mass % of propene in the initial monomeric mixture are given as an example in Figure 9. The curves represented by broken lines were calculated directly from chromatographic data.

The known time dependences of the chromatographically determined amount of monomers in the sample (Figs. 3–8) were also used in the calculation of the initial reaction rates of both monomers. The results are summarized in Table I. Chromatographic results obtained in the copolymerization of vinyl chloride with various contents of comonomer may at the same time be utilized in the determination of the copolymerization parameters. The copolymerization parameters  $r_1, r_2$  of the vinyl chloride–propene system were calculated by the Fineman–Ross method.<sup>5</sup> The individual terms of the equation

$$a - a/b = r_1 a^2/b - r_2 \quad (1)$$

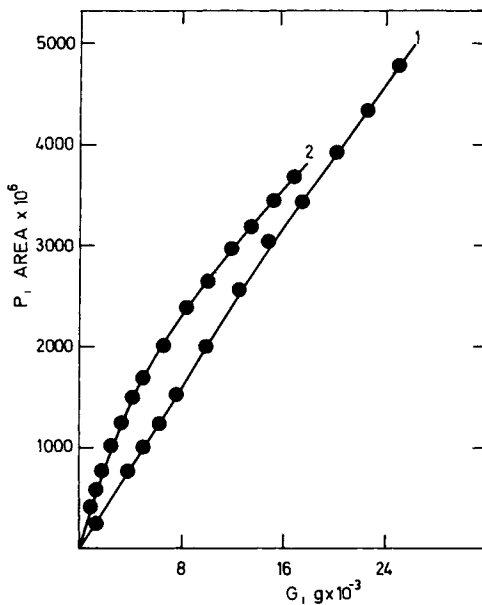


Fig. 2. Calibration plot for vinyl chloride (1) and propene (2) (AREA is the response of a flame-ionization detector).

were calculated by substituting for  $a$  the ratio of the molar concentrations of vinyl chloride and propene at the beginning of copolymerization determined chromatographically or gravimetrically from the known composition of the initial

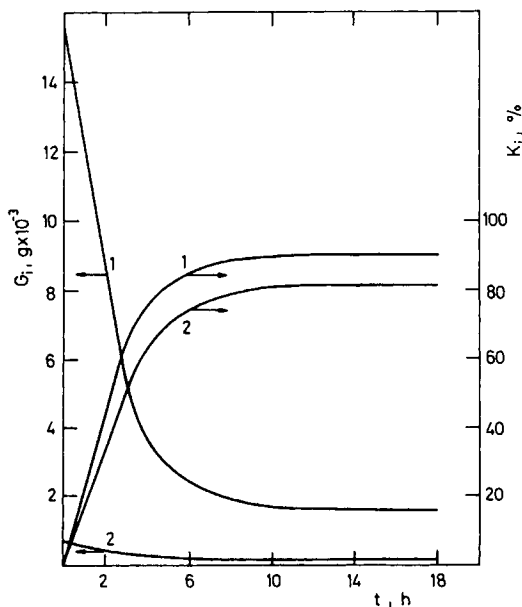


Fig. 3. Time dependence of the chromatographically determined amount of monomers ( $G_i$ ) in the sample and of the degree of conversion ( $K_i$ ) reached for 5.3 mass % of propene in the initial monomeric mixture: (1) vinyl chloride; (2) propene; index  $i$  holds for the respective monomer 1 or 2.

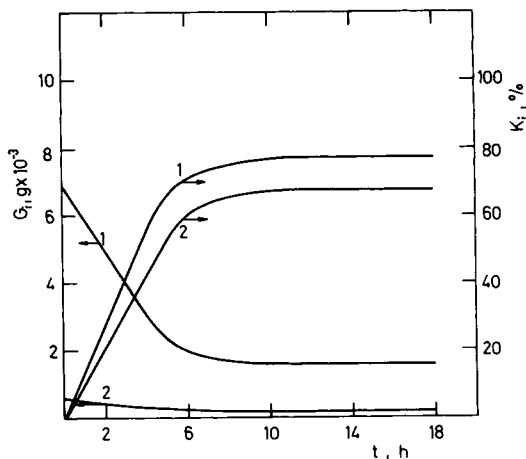


Fig. 4. Time dependence of the chromatographically determined amount of monomers ( $G_i$ ) in the sample and of the degree of conversion ( $K_i$ ) reached for 10.4 mass % of propene in the initial monomeric mixture. For the meaning of the symbols, cf. Figure 3.

monomeric mixture, and for  $b$  directly the ratios of the initial reaction rates of both monomers expressed in moles of the respective monomer and related to liter and second. The initial reaction rates were determined from chromatographic data. The resulting regression curves were determined by the least squares method. The results are reviewed in Table II. Some further results of the copolymerizations of vinyl chloride with propene are listed in Table III.

## DISCUSSION

### Comparison of the Final Degrees of Conversion Determined Chromatographically and Gravimetrically

Results of the final chromatographically determined conversions of a series of the copolymerizations of vinyl chloride with propene are higher by 5–9% rel than values obtained gravimetrically.

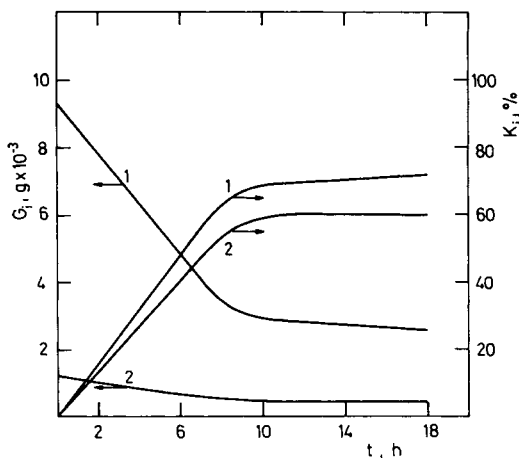


Fig. 5. Time dependence of the chromatographically determined amount of monomers ( $G_i$ ) in the sample and of the degree of conversion ( $K_i$ ) reached for 14.4 mass % of propene in the initial monomeric mixture. For the meaning of the symbols, cf. Figure 3.

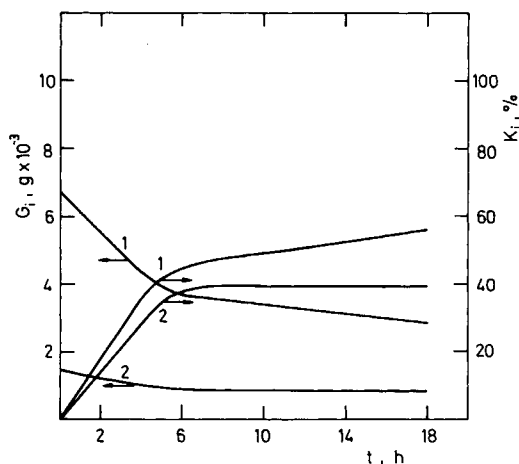


Fig. 6. Time dependence of the chromatographically determined amount of monomers ( $G_i$ ) in the sample and of the degree of conversion ( $K_i$ ) reached for 20.2 mass % propene in the initial monomeric mixture. For the meaning of the symbols, cf. Figure 3.

The difference ensues from the nature of the suggested method which—as has already been said—in the calculation of conversions employs the mass balance only of monomers present in the heterogeneous reaction mixture, unlike the gravimetric method. The chromatographically determined conversions were therefore corrected with respect to the amount of monomers present in the gas phase and to the losses arising in the sampling of the gas phase.

The amount of the monomers present in the vapor space of the reactor was calculated so that the average molecular mass of the gas phase and the average density of the liquid phase were determined from the composition of the gas and liquid phases. The equilibrium liquid–vapor diagrams were used in checking the composition and mass fraction of the gas and heterogeneous liquid phases at the beginning and during the copolymerization.

The amount of monomers present in the gas phase at the beginning of co-

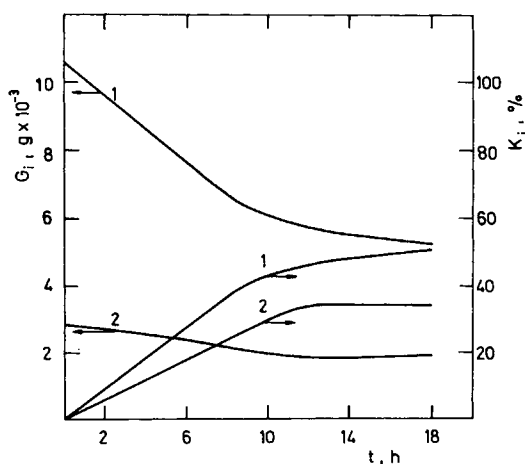


Fig. 7. Time dependence of the chromatographically determined amount of monomers ( $G_i$ ) in the sample and the degree of conversion ( $K_i$ ) reached for 24.3 mass % of propene in the initial monomeric mixture. For the meaning of the symbols, cf. Figure 3.

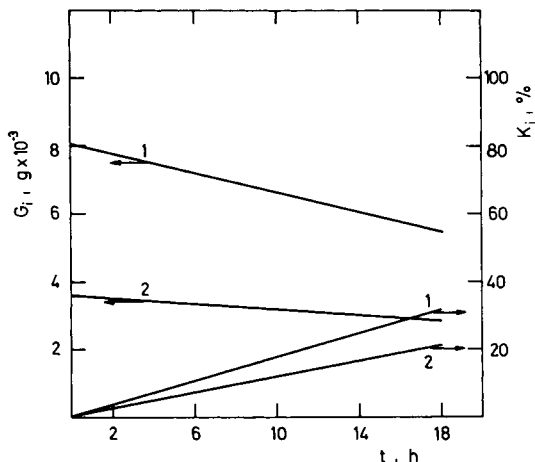


Fig. 8. Time dependence of the chromatographically determined amount of monomers ( $G_i$ ) in the sample and the degree of conversion ( $K_i$ ) reached for 30.5 mass % of propene in the initial monomeric mixture. For the meaning of the symbols, cf. Figure 3.

polymerization,  $G^0_{(g)}$ , and at a time  $t$ ,  $G^t_{(g)}$ , was calculated assuming that the following mass balance,

$$G^0 = G^0_{(g)} + G^0_{(l)} \quad (2)$$

$$G^t = G^t_{(g)} + G^t_{(l)} + G^t_{(s)} \quad (3)$$

is valid. In eqs. (2) and (3),  $G_{(l)}$  and  $G_{(s)}$  respectively denote the mass amounts of monomers in the liquid phase and the amount of the copolymer formed. By using the procedure outlined above, a general relation can be derived for the calculation of the mass fraction of monomers in the gas phase at the beginning of copolymerization ( $X^0$ ) and during the process ( $X^t$ ):

$$G^0 = (V_R - V_{H_2O}) \cdot \left[ X^0 \cdot \left( \frac{P^0 \cdot \bar{M}^0_{(g)}}{R \cdot T} - \bar{s}^0_{(l)} \right) + \bar{s}^0_{(l)} \right], \quad (4)$$

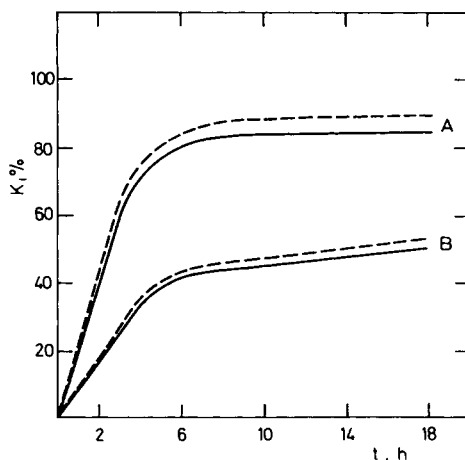


Fig. 9. Summary conversion curves of the copolymerization of vinyl chloride with propene constructed using chromatographic data directly (---) and after recalculation (—); (A) 5.3 mass % and (B) 20.2 mass % of propene in the initial monomeric mixture.

TABLE I  
Initial Reaction Rates of Both Monomers Determined in Copolymerization of Vinyl Chloride with Propene

$[P]_0^a$ (mol %)	$-\Delta[\text{VCM}]/\Delta t$ ( $10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ )	$-\Delta[P]/\Delta t$ ( $10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ )
7.9	30.2	1.4
14.8	8.4	0.8
19.9	6.6	1.1
27.4	5.3	1.3
32.3	4.3	1.1
39.5	1.3	0.6

<sup>a</sup> Propene content in the initial monomeric mixture.

$$G^t = \left( V_R - V_{\text{H}_2\text{O}} + \frac{G^0 \cdot K}{s_{(s)}} \right) \cdot \left[ X^t \cdot \left( \frac{P^t \cdot \bar{M}^t_{(g)}}{R \cdot T} - \bar{s}^t_{(l)} \cdot (1 - K) \right) + \bar{s}^t_{(l)} \cdot (1 - K) \right], \quad (5)$$

where  $V_R$  is the reactor volume (L),  $V_{\text{H}_2\text{O}}$  is the volume of water in the reactor (L),  $P^0$ ,  $P^t$ , respectively, are the pressures at the beginning of and during the copolymerization (MPa),  $\bar{M}^0_{(g)}$ ,  $\bar{M}^t_{(g)}$  are the respective average molecular masses of the gas monomeric mixture,  $R$  is the gas constant (MPa · L/mol · grad),  $T$  is temperature (°K),  $\bar{s}^0_{(l)}$ ,  $\bar{s}^t_{(l)}$  is the average density of the liquid phase (kg/L),  $s_{(s)}$  is the specific mass of the copolymer (kg/L), and  $K$  is conversion.

TABLE II  
Copolymerization Parameters for Vinyl Chloride-Propene System

Experimental values				Literary data	
$a^a$		$a^b$		VCM	P
VCM	P	VCM	P	VCM	P
1.8	0.9	1.2	0.6	2.2	0.2 <sup>6</sup>
				2.3	0.3 <sup>6</sup>
				2.9	0.0 <sup>7</sup>

<sup>a</sup>  $a$  determined gravimetrically [cf. eq. (1)].

<sup>b</sup>  $a$  determined chromatographically.

TABLE III  
Results of Copolymerizations of Vinyl Chloride with Propene Lasting 18 h

$[P]_0^a$ (mol %)	$\{P\}^b$ (mol %)	$K_{GC}^c$ (%)	$K_W^d$ (%)	$[\eta]^e \times 10^{-2}$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	$A^f$ (% from yield)
7.9	3.1	89.6	84.0	0.658	3.3
14.8	5.5	76.5	70.4	0.614	3.9
19.9	7.6	70.7	65.3	0.497	2.6
27.4	9.7	53.7	50.1	0.416	5.0
32.3	11.2	47.5	43.3	0.327	3.7
39.5	14.4	28.5	27.1	0.315	13.2

<sup>a</sup> Propene content in the initial monomeric mixture.

<sup>b</sup> Propene content in the copolymer.

<sup>c</sup> Final total conversion of monomers determined chromatographically.

<sup>d</sup> Final total conversion of monomers determined gravimetrically.

<sup>e</sup> Intrinsic viscosity.

<sup>f</sup> Residue on the sieve 0.250 mm.



Knowing  $X^0$  and  $X^t$ , it is possible to calculate the mass amounts of monomers in the gas phase using the relations

$$G^0_{(g)} = (V_R - V_{H_2O}) \cdot \left( X^0 \frac{P^0 \cdot \bar{M}^0_{(g)}}{R \cdot T} \right) \quad (6)$$

$$G^t_{(g)} = \left( V_R - V_{H_2O} + \frac{G^0 \cdot K}{s_{(s)}} \right) \cdot \left( X^t \frac{P^t \cdot \bar{M}^t_{(g)}}{R \cdot T} \right) \quad (7)$$

It was found that at the beginning of a copolymerization the amount of monomers in the gas phase is 3.8–3.9% rel. With increasing degree of conversion the monomer content in the gas phase increases to 4.8–5.8% rel at the given filling of the reactor, or under the given experimental conditions. Within 0–30 mass % of propene these values depend very little on the composition of the initial monomeric mixture.

Losses arising in the sampling of the gas phase vary between 0.2 and 0.4% rel, depending on the number of samplings, the volumes taken, and the composition of the gas phase.

Hence, correction of chromatographic data in order to estimate the agreement between the calculated conversion and gravimetric results must take into account the amount of monomers present in the gas space of the reactor at the beginning of the reaction, and also reflect the fact that, in the following stage of the reaction, monomers from the liquid phase pass into this space which becomes extended because of the volume contraction of the reaction mixture. The calculations show that differences between the chromatographic and gravimetric determinations of conversion due to the presence of monomers in the gas phase and to losses which occur in the sampling of the gas phase vary in the range 5.0–6.2% rel. The real value depends on the degree of conversion reached and on the amount of the gas phase taken for sampling. The corrections just discussed are respected in curve 1, Figure 10, the slope of which includes the average correction 5.6% rel. This value was used in the correction of curves obtained chromatographically (Fig. 9) and of the final conversions determined chromatographically

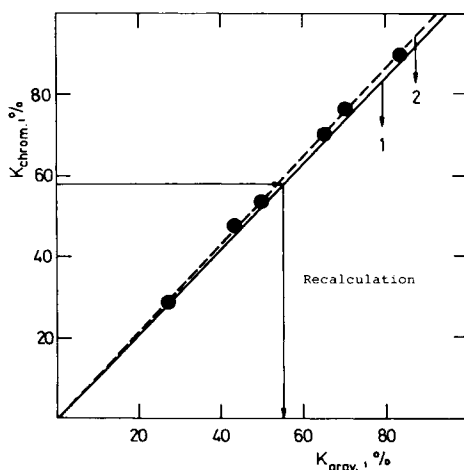


Fig. 10. Relationship between the degrees of conversion determined chromatographically and gravimetrically in the copolymerization of vinyl chloride with propene: (1) theoretical correction straight line; (2) experimental straight line.

in a series of copolymerizations of vinyl chloride containing various amounts of propene. The comparison is shown in the following Table IV. It can be seen in Table IV that differences between the corrected conversion determined chromatographically and conversion determined gravimetrically do not exceed 2% on the average.

Experimental points which represent intersections of final conversions determined directly by the chromatographic method (without recalculation) and by the classical gravimetric method lie on straight line 2 in Figure 10. The mutual position of straight lines 1 and 2 indicates good fit between the results obtained by the new method, on the one hand, and gravimetric values, on the other.

### Kinetic Course of the Copolymerization of Vinyl Chloride with Propene

The dependences in Figures 3–8 show that with increasing content of propene in the initial monomeric mixture the copolymerization process is markedly slowed down and that the autoacceleration effect, typical of the homopolymerization of vinyl chloride,<sup>8</sup> is eliminated already at low concentrations of propene. The instantaneous degrees of conversion of propene at any reaction time are lower than those of vinyl chloride; as a consequence, the relative content of this comonomer increases in the reaction mixture during the reaction. Changes in the reaction pressure, which can easily be observed due to the great difference in the tensions of saturated vapors of both monomers, also are a consequence of changes in the composition of the reaction mixture. If the relation between pressure and conversion for a given composition of the initial monomeric mixture is experimentally known, the pressure record can be utilized in an estimate of the instantaneous degree of conversion.

A closer quantitative insight into the copolymerization process was provided by the initial reaction rates (Table I). The initial reaction rate of vinyl chloride markedly decreases with increasing concentration of 1-olefin in the initial monomeric mixture. The initial reactions rates of propene are always lower than those of vinyl chloride and virtually independent of the composition of the initial monomeric mixture.

TABLE IV  
Comparison of Final Conversions

$[P]_0$ (% mol)	$K_{GC}$ (%)	$K_{GC\ corr}^a$ (%)	$K_W$ (%)	$K_{GC\ corr} - K_W$ (%)
7.9	89.6	84.6	84.0	0.6
14.8	76.5	72.2	70.4	1.8
19.9	70.7	66.7	65.3	1.3
27.4	53.7	50.7	50.1	0.6
32.3	47.5	44.8	43.3	1.5
39.5	28.5	26.9	27.1	-0.2

<sup>a</sup> Chromatographic conversion, corrected

### Determination of the Copolymerization Parameters

The results summarized in Table II confirm that the suggested application of the new method is also suited for the determination of the copolymerization parameters. In view of the fact that the chromatographic determination adequately reflects the content of both monomers in the liquid phase and thus also the processes by which the copolymerization parameters are predominantly determined, the use of chromatographic data in the application of the suggested method seems more objective compared with gravimetric data (Table II).

### Further Results of the Copolymerizations of Vinyl Chloride with Propene

The propene contents in the copolymer given in Table III are based on the determination of carbon by elemental analysis. Repeated analyses performed with the same samples showed that the determination of carbon is subjected to a smaller error than that of chlorine. In addition to the speed and accuracy of the determination, such a choice was also motivated by the fact that dehydrochlorination changes (if any) occurring in the polymer chain do not affect the determination.

The intrinsic viscosities of solutions of copolymers prepared in this study decrease with the increasing content of propene in the initial monomeric mixture or in the copolymer. This trend may be a consequence of the decreased reactivity of the end propene radical and of the increased participation of transfer reactions in the overall reaction mechanism.

### CONCLUSIONS

In a series of copolymerizations of vinyl chloride with propene, it has been confirmed that a method suggested earlier<sup>1</sup> and based on periodic sampling of a heterogeneous reaction mixture from the reactor during the reaction and on the gas-chromatographic determination of unreacted monomers present in the sample is suited not only for an investigation of the course of homopolymerization of vinyl chloride,<sup>1</sup> but also for a study of its copolymerization with propene. By employing this method, the summary conversion copolymerization curves and conversion curves of the individual monomers were constructed, their initial reaction rates were calculated and the copolymerization parameters were determined. With the exception of the copolymerization parameters, all these data were derived from a single experiment for a given composition of the monomeric mixture copolymerized according to a chosen working instruction.

The procedure is only a little time-consuming and at the same time provides results which give a more detailed insight into the copolymerization reaction of vinyl chloride with propene.

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