Influence of pressure on the copolymerization of ethylene and vinylacetate : determination of the kinetics by the "sandwich" method

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INFLUENCE OF PRESSURE ON THE COPOLYMERIZATION OF ETHYLENE AND VINYLACETATE

Determination of the kinetics by the "sandwich" method

F. DE KOK

INFLUENCE OF PRESSURE ON THE COPOLYMERIZATION OF ETHYLENE AND VINYLACETATE

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL TE EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. IR. G. VOSSERS, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VAN DECANEN IN HET OPENBAAR TE VERDEDIGEN OP VRIJDAG 24 NOVEMBER 1972 TE 16.00 UUR

DOOR

FRANS DE KOK
GEBOREN TE AMERSFOORT

DRUKKERIJ J. H. PASMANS. 'S-GRAVENHAGE

DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOREN

PROF. DR. D. HEIKENS

EN

PROF. DR. J. SCHUYER

Aan mijn moeder
Aan wijlen mijn vader
Aan mijn vrouw

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6 INFLUENCE OF TEMPERATURE ON THE *r*-VALUES

7 EXAMINATION OF THE PHASE BEHAVIOUR OF THE SYSTEM ETHYLENE - VINYLACETATE - *ISO*-PROPYLALCOHOL - COPOLYMER

8 INFLUENCE OF *ISO*-PROPYLALCOHOL ON THE KINETICS

CHAPTER 1

INTRODUCTION

In the thesis of A.L. German (ref. 1) the basis has been laid for an investigation concerning the influence of pressure on the copolymerization of ethylene with vinylacetate by reacting these monomers in *tert*-butylalcohol at low pressure (35 kg/cm^2) and 62^{o}C.
References mentioned in the above thesis show the uncertainty and inaccuracy of copolymerization data at that time. With exception of the work of German the picture has not been changed much.
The influence of pressure on the so-called monomer reactivity ratios (*r*-values) and the values of these ratios were uncertain, not only because of the analytical techniques used and the possibility of the absence of a stationary state during the whole experiment, but also because of the possibility of phase separations in the investigations of the different authors. These separations forbid the use of simple mass law equations.

German followed the kinetics of the system by determining the concentrations of monomers and solvent by sequential sampling and accurate gas chromatographic analysis. Thus he convinced himself that the data used for the determination of the kinetics correspond with the stationary state stage of the experiment.
The large number of accurate experimental data supplied by each kinetic run and the large number of runs at different monomer feed ratios together with a computer program for the determination of *r*-values by non-linear least-squares methods, guaranteed the reliability and accuracy of his results. All data fitted the Alfrey model description extremely well.

In the work described in the present thesis reactions were carried out at high-pressures (600 kg/cm^2) and 62°C. The data were gathered in an indirect way in so-called "sandwich" experiments, to be discussed later on in Chapter 5. The *r*-values have been obtained by a computational procedure for evaluation comparable with that used by German. In Appendix II small systematic deviations in the data and *r*-values will be explained by appropriate hypothesis based on analytical observations.
For reasons of *r*-value correction the knowledge of the influence of temperature on this copolymerization seemed to be a necessity and appropriate measurements will be described in Chapter 6.

A device developed for direct sampling of monomers and solvent from a vessel under high pressure is described in Appendix III. Low-pressure experiments (35 kg/cm^2) at 62°C, by which this device has been tested, resulted in data of a somewhat lower accuracy, because of absorption of volatile components in the sample at copolymer deposited in the evaporation chamber of the valve.

The device will work well for reactions in which no polymers are present. After small modifications it is expected to work well for reactions in which polymers are formed.

Future copolymerizations are planned to be carried out at still higher pressure (over 3000 kg/cm^2) where indications of phase separations have been found in experiments at the Physics Department of the Delft University of Technology *). Results of these experiments can be found in Chapter 7. Although all experiments in this thesis have

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*) The experiments were carried out with kind permission of Prof. Dr. Ir. G.A.M. Diepen.

been carried out in *tert*-butylalcohol at 600 kg/cm^2, *iso*-propylalcohol was thought to be a better solvent at still higher pressure. Therefore, a separate series of copolymerizations has been performed in the latter solvent at 35 kg/cm^2 and 62°C, to form the base of future research. The results are to be found in Chapter 8 and they are very near to those of German in *tert*-butylalcohol. Small solvent effects could be traced back to solvent transfer reactions and will be discussed.

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CHAPTER 2

FREE-RADICAL POLYMERIZATION OF VINYL MONOMERS

2.1 BASIC EQUATIONS

A generally accepted model describing the free-radical copolymerization is given by Mayo and Lewis (ref. 1) and Alfrey and Goldfinger (ref. 2).
German (ref. 3) proved the validity of the model over a wide concentration range of the system ethylene and vinylacetate with the aid of an integral equation that contains monomer feed ratio and the conversion of one of the monomers as the only variables.

In view of the "sandwich" method described in Chapter 5 an equation of monomer feed ratio and time has been derived, describing monomer feed ratio as a function of reaction time.

2.1.1 COPOLYMERIZATION EQUATIONS

German (ref. 3) derived the copolymerization equation under the following main conditions:

- Initiation, termination and transfer steps play no part and only propagation steps should be considered; which has to be confirmed by a sufficiently high molecular weight of the copolymer products.

- Propagation rate does not depend on the chain length, penultimate effects or anomalous additions.

- The law of mass action holds.

The derivation of the copolymerization equation does not require a constant reaction volume (ref. 3) and considers the four propagation reactions:

$\sim a. + a \longrightarrow \sim a.$ with rate constant k_{aa}
$\sim a. + b \longrightarrow \sim b.$ with rate constant k_{ab}
$\sim b. + a \longrightarrow \sim a.$ with rate constant k_{ba}
$\sim b. + b \longrightarrow \sim b.$ with rate constant k_{bb}

where $\sim a.$ and $\sim b.$ are polymer chains ending with radicals formed of the monomers a and b .

Hence we get the following copolymerization equation:

$$\frac{dn_a}{dn_b} = \frac{r_a \dfrac{n_a}{n_b} + 1}{r_b \dfrac{n_b}{n_a} + 1} \qquad (2\text{-}1)$$

in which n_a = number of moles "a" in the reactor,
n_b = number of moles "b" in the reactor,
r_a and r_b are the monomer reactivity ratios,
$r_a = k_{aa}/k_{ab}$,
$r_b = k_{bb}/k_{ba}$.

For the point of time t_i rearrangement of (2-1) yields:

$$\frac{d \ln q_i}{d \ln (f_b)_i} = \frac{q_i * r_a + 1}{r_b + q_i} - 1 \qquad (2\text{-}2)$$

in which $q_i = \left(\dfrac{n_a}{n_b}\right)_i$,

$$(f_b)_i = \frac{(n_b)_i}{(n_b)_o} ,$$

$(n_b)_o$ = initial number of moles "b" in the reactor .

Integration of equation (2-2) between the co-ordinates

$$(f_b)_i \ , \ (q)_i \ ,$$

and

$$(f_b)_j \ , \ (q)_j \ ,$$

under condition that

$$r_a \neq 1 \ ,$$

$$r_b \neq 1 \ ,$$

and

$$q \neq \frac{r_b - 1}{r_a - 1} \ ,$$

yields the integrated version of the copolymerization equation

$$\frac{r_b}{r_b-1} \ln \frac{q_j(R+q_i)}{q_i(R+q_j)} + \frac{1}{1-r_a} \ln \frac{q_j+R}{q_i+R} - \ln \frac{100-F_b}{100} = 0 \qquad (2\text{-}3)$$

in which

$$q_i = \left(\frac{n_a}{n_b}\right)_i , \ q_j = \left(\frac{n_a}{n_b}\right)_j , \ R = \frac{r_b-1}{1-r_a} \text{ and } F_b = 100 * \left\{ 1 - \frac{(f_b)_i}{(f_b)_j} \right\} ,$$

while the value of $(n_b)_o$ is arbitrary, as

$$\frac{(f_b)_j}{(f_b)_i} = \frac{(n_b)_j}{(n_b)_i} \ .$$

Equation (2-3) connects the monomer feed ratio q with the relative conversion F_b based on one of the monomers.

Except for the initial integration limit $(f_b)_i \neq 1$ and $q_i \neq q\left((f_b)_i = 1\right)$, and the arrangements made in connection with the specific parameters arising from the experiments described in this thesis, equation (2-3) corresponds with integrated forms derived by other investigators (ref. 1, 3, 5, 6, 7).

2.1.2 EQUATION OF MONOMER FEED RATIO AND TIME

An equation of monomer feed ratio and reaction time can be derived under condition that:

- The contribution of initiation and termination steps to the entire monomer consumption is almost negligible. The contribution of transfer steps to the entire monomer consumption is negligible.
  This has to be confirmed by a sufficiently high molecular weight of the copolymer products.

- Propagation rate does not depend on chain length, penultimate effects or anomalous additions.

- The law of mass action holds.

- The "steady-state" holds for each type of free radical.

- The termination step takes place only by combination of free radicals, as in case of vinyl (co-)polymerizations (ref. 4).

The derivation applies to the following reactions:

- Decomposition of the initiator I

  $I \longrightarrow 2\,R\cdot$ with rate constant k_d ;

- Initiation of the monomers by the initiator radical R.

  R. + a $\rightarrow$ ∿a. with rate constant k_{ia} ,

  and R. + b $\rightarrow$ ∿b. with rate constant k_{ib} ;

- Propagation described in 2.1.1;

- Termination by combination

  ∿a. + ∿a. $\rightarrow$ ∿ with rate constant k_{taa} ,

  ∿a. + ∿b. $\rightarrow$ ∿ with rate constant k_{tab} ,

  and ∿b. + ∿b. $\rightarrow$ ∿ with rate constant k_{tbb} .

During an experiment, reaction time t changes and reaction volume V changes because of contraction. Consequently:

$$q = q(t, V(t)) \ ,$$

and

$$dq = \left(\frac{\partial q}{\partial t}\right)_V dt + \left(\frac{\partial q}{\partial V}\right)_t \frac{dV}{dt}\, dt$$

Because $\left(\frac{\partial q}{\partial V}\right)_t = 0$, the relation between monomer feed ratio and time may be derived assuming a constant reaction volume. Therefore, the equation will be derived using numbers of moles.

The "steady-state" assumption

This assumption leads to

$$k_{ab} * a. * n_b = k_{ba} * b. * n_a \tag{2-4}$$

$$\frac{da.}{dt} \simeq 0 \ , \tag{2-5a}$$

$$\frac{db.}{dt} \simeq 0 \ , \tag{2-5b}$$

and

$$\frac{dR^{\bullet}}{dt} \simeq 0 \ . \tag{2-5c}$$

$a.$, $b.$ and $R^{\bullet}$ being the numbers of moles of the free-radicals ∿a., ∿b. and R. .

Monomer consumption

A sufficiently high molecular weight of the copolymer product will guarantee that monomers are almost exclusively consumed by propagation reactions:

$$-\frac{dn_a}{dt} = k_{aa} * a. * n_a + k_{ba} * b. * n_a \qquad (2\text{-}6a)$$

$$-\frac{dn_b}{dt} = k_{bb} * b. * n_b + k_{ab} * a. * n_b \qquad (2\text{-}6b)$$

$$\frac{d(n_a/n_b)}{dt} = \frac{n_a}{n_b} * \left(\frac{1}{n_a}\frac{dn_a}{dt} - \frac{1}{n_b}\frac{dn_b}{dt}\right) \qquad (2\text{-}7)$$

Combination of equations (2-4), (2-6a), (2-6b) and (2-7) gives:

$$\frac{dq}{dt} = k_{ab} * (1-r_a) * (q+R) * a. \qquad (2\text{-}8)$$

Next the number of radicals $a.$ will be derived from the initiator- and the chain-radical production, and an equation will be reached that contains measurable quantities.

Initiator-radical production

The decomposition of the initiator I is described by a first order reaction.
Consequently:

$$I(t) = I_o \exp(-k_d * t) \qquad (2\text{-}9)$$

in which I_o = initial number of moles "I" in the reactor.

The consumption and production of initiator-radicals is described by:

$$\frac{dR^{\bullet}_{\cdot}}{dt} = 2 * \alpha * k_d * I(t) - (k_{ia} * n_a + k_{ib} * n_b) * R^{\bullet}_{\cdot} \qquad (2\text{-}10)$$

in which α = efficiency of the initiator.

Combination of equations (2-5c), (2-9) and (2-10) yields:

$$R^{\bullet}_{\cdot} = \frac{2 * \alpha * k_d * I_o}{k_{ia} * n_a + k_{ib} * n_b} \exp(-k_d * t) \qquad (2\text{-}11)$$

<u>Chain-radical production</u>

The chain-radical production is governed by initiation, propagation and termination steps.
Consequently:

$$\frac{da.}{dt} = k_{ia} * R^{\bullet}_{\cdot} * n_a - 2 * k_{taa} * a.^2 - k_{tab} * a. * b.$$

$$+ k_{ba} * b. * n_a - k_{ab} * a. * n_b \qquad (2\text{-}12a)$$

An analogous equation holds for $\frac{db.}{dt}$. (2-12b)

Combination of (2-5a) and (2-12a) yields, with allowed neglections for high molecular copolymer formed:

$$a. = \frac{k_{ia} * R^{\bullet}_{\cdot} + k_{ba} * b.}{k_{ab} * n_b + k_{tab} * b.} * n_a \qquad (2\text{-}13a)$$

Combination of (2-5b) and (2-12b) yields analogously:

$$b. = \frac{k_{ib} * R^{\bullet}_{\cdot} + k_{ab} * a.}{k_{ba} * n_a + k_{tab} * a.} * n_b \qquad (2\text{-}13b)$$

Substitution of $b.$ according to (2-13b) into (2-13a) yields by approximation after rearranging:

$$a. \;=\; \left(\frac{(k_{ia} * n_a + k_{ib} * n_b) * k_{ba} * n_a * R^{\bullet}}{2 * k_{ab} * k_{tab} * n_b} \right)^{\frac{1}{2}} \qquad (2\text{-}14)$$

Differential equation of monomer feed ratio and time

Combination of equation (2-8), (2-11) and (2-14) yields:

$$\frac{dq}{dt} = P * (q+R) * q^{\frac{1}{2}} * I_o \exp(-\tfrac{1}{2} * k_d * t) \qquad (2\text{-}15)$$

in which $P = (1-r_a) * k_{ab} * \left(\frac{\alpha * k_d * k_{ba}}{k_{tab} * k_{ab}} \right)^{\frac{1}{2}}$.

Integral equation of monomer feed ratio and time

The differential equation of monomer feed ratio and time (2-15) can be integrated and will thus yield a relation between the monomer feed ratio and the reaction-time. Equation (2-15) can be rearranged to:

$$\frac{dq}{(q+R) * q^{\frac{1}{2}}} = P * I_o^{\frac{1}{2}} * \exp(-\tfrac{1}{2} * k_d * t)\; dt$$

Integration between the co-ordinates $t = t_i$ and $q = q_i$, and the co-ordinates $t = t_j$ and $q = q_j$, yields:

$$\sin^{-1} \left(\frac{q_i - R}{q_i + R} \right) - \sin^{-1} \left(\frac{q_j - R}{q_j + R} \right) =$$

$$= S * \left\{ \exp(-\tfrac{1}{2} * k_d * t_i) - \exp(-\tfrac{1}{2} * k_d * t_j) \right\} \qquad (2\text{-}16)$$

in which $S = (r_a - 1) * \left(I_o * R * \frac{\alpha * k_{ab} * k_{ba}}{k_{tab} * k_d} \right)^{\frac{1}{2}}$,

and $R = \frac{r_b - 1}{1 - r_a} > 0$.

The importance of this equation is that it describes the copolymerization of ethylene and vinylacetate as a function of reaction-time. Together with the copolymerization equation (2-3) it will be used in the "sandwich" method for extrapolation purposes (cf. Chapter 5).

2.2 EFFECTS OF TEMPERATURE AND PRESSURE ON THE MONOMER REACTIVITY RATIOS

Starting from the theory of transition state, the reaction rate may be described by (ref. 8):

$$k = \exp\,(-\,\Delta G^{\#}/RT) \tag{2-17}$$

in which k = reaction rate,
$\Delta G^{\#}$ = the difference between the free enthalpy of the "activated complex" and the reactants, briefly indicated as free enthalpy of activation,
R = gas constant,
T = absolute temperature.

The effect of temperature on the reaction rate is described by the thermodynamic equation (ref. 8, 9):

$$\frac{d(\ln\ k)}{dT} = \frac{\Delta H^{\#}}{RT^2} \tag{2-18}$$

in which $\Delta H^{\#}$ = difference in the enthalpy of the "activated complex" and the reactants.

The pressure dependence of the reaction rate is governed by the activation volume $\Delta V^{\#}$ described by the thermodynamic equation (ref. 9, 10):

$$\frac{d(\ln k)}{dp} = -\frac{\Delta V^{\#}}{RT} \tag{2-19}$$

in which $\Delta V^{\#}$ = the difference between the volume of the "activated complex" and the reactants, briefly indicated as activation volume.

The effects of temperature and pressure on the monomer reactivity ratios will now be derived.

The contributions of the partial activation volume of the monomers and of the monomer radicals to the activation volume will be discussed.

A scheme of correlation, the monomer activation volume scheme, will be proposed. It describes the influence of pressure in a general and quantitative way.

2.2.1 EFFECT OF TEMPERATURE

Using equation (2-17) the reactivity ratio r_a may be expressed as:

$$r_a = \frac{k_{aa}}{k_{ab}} = \exp\left(-\frac{\Delta G_{aa}^{\#} - \Delta G_{ab}^{\#}}{RT}\right) \tag{2-20}$$

in which $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$,
$\Delta H^{\#}$ = enthalpy of activation,
and $\Delta S^{\#}$ = entropy of activation.

The calculation of r_a-values at various temperature levels is possible if the equation derived from (2-20) is used:

$$(r_a)_{T_2} = (r_a)_{T_1} \exp\left\{ - \frac{\Delta H_{aa}^{\#} - \Delta H_{ab}^{\#}}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\} \qquad (2\text{-}21)$$

Similar expressions hold for r_b .

2.2.2 EFFECT OF PRESSURE

Using equation (2-19) the pressure dependence of the reactivity ratio r_a may be expressed as:

$$\frac{d \ln r_a}{dp} = - \frac{\Delta V_{aa}^{\#} - \Delta V_{ab}^{\#}}{RT} \qquad (2\text{-}22)$$

The r_a-values at various pressures are correlated by the integrated version of equation (2-22):

$$(r_a)_{p_2} = (r_a)_{p_1} \exp\left\{ - \frac{\Delta V_{aa}^{\#} - \Delta V_{ab}^{\#}}{RT} * (p_2 - p_1)\right\} \qquad (2\text{-}23)$$

Similar expressions hold for r_b .

2.2.3 PARTIAL ACTIVATION VOLUMES

The activation volume of homopropagation and cross-propagation reactions may be expressed as an addition of partial activation volumes of monomers and monomer radicals:

$$\Delta V_{aa}^{\#} = (\Delta V_{a.}^{\#})_{a} + (\Delta V_{a}^{\#})_{a.} \qquad (2\text{-}24\text{-}a)$$

$$\Delta V_{ab}^{\#} = (\Delta V_{a.}^{\#})_{b} + (\Delta V_{b}^{\#})_{a.} \qquad (2\text{-}24\text{-}b)$$

$$\Delta V_{bb}^{\#} = (\Delta V_{b.}^{\#})_{b} + (\Delta V_{b}^{\#})_{b.} \qquad (2\text{-}24\text{-}c)$$

$$\Delta V_{ba}^{\#} = (\Delta V_{b.}^{\#})_{a} + (\Delta V_{a}^{\#})_{b.} \qquad (2\text{-}24\text{-}d)$$

Assuming that the volumetric contributions of the monomers and the radicals to the volume of activation of the different transition states are independent of the kind of transition state formed, it follows that:

$$(\Delta V_{a.}^{\#})_{a} = (\Delta V_{a.}^{\#})_{b} = \Delta V_{a.}^{\#} \qquad (2\text{-}25\text{-}a)$$

$$(\Delta V_{b.}^{\#})_{a} = (\Delta V_{b.}^{\#})_{b} = \Delta V_{b.}^{\#} \qquad (2\text{-}25\text{-}b)$$

$$(\Delta V_{a}^{\#})_{a.} = (\Delta V_{a}^{\#})_{b.} = \Delta V_{a}^{\#} \qquad (2\text{-}25\text{-}c)$$

$$(\Delta V_{b}^{\#})_{a.} = (\Delta V_{b}^{\#})_{b.} = \Delta V_{b}^{\#} \qquad (2\text{-}25\text{-}d)$$

Combination of equations (2-22), and (2-25-a to d) yields:

$$\frac{d \ln r_{a}}{dp} = - \frac{\Delta V_{a}^{\#} - \Delta V_{b}^{\#}}{RT} \qquad (2\text{-}26\text{-}a)$$

and

$$\frac{d \ln r_{b}}{dp} = + \frac{\Delta V_{a}^{\#} - \Delta V_{b}^{\#}}{RT} \qquad (2\text{-}26\text{-}b)$$

Consequently:

$$\frac{d \ln (r_{a} * r_{b})}{dp} = 0 \qquad (2\text{-}27)$$

If equations (2-25-a) to (2-25-d) hold, the r-values will, according to equations (2-26-a), (2-26-b) and (2-27), change with increasing pressure in opposite directions with $r_{a} * r_{b}$ = constant.

If the activation volume cannot be described as the sum of independent partial volumes, it can be expected that *at least* the sign of $\frac{d \ln r_a}{dp}$ is opposite to $\frac{d \ln r_b}{dp}$.

2.2.4 PARTIAL ACTIVATION ENERGIES

Arguments, similar to those for partial activation volumes, hold for partial activation energies.

2.2.5 THE HYPOTHETIC MONOMER ACTIVATION VOLUME SCHEME

Under condition that equation (2-27) holds universally, the hypothetic monomer activation volume scheme may be set up.

The difference between the two partial monomer activation volumes ΔV_{ab}^{*}, as evaluated from experiments, describes the pressure dependence of the r-values for a system of two monomers a and b :

$$\Delta V_{ab}^{*} = \Delta V_{a}^{\#} - \Delta V_{b}^{\#} \tag{2-28}$$

Similarly for the monomers b and c :

$$\Delta V_{bc}^{*} = \Delta V_{b}^{\#} - \Delta V_{c}^{\#} \tag{2-29}$$

These results allow predictions for the system of the monomers a and c:

$$\Delta V_{ac}^{*} = \Delta V_{a}^{\#} - \Delta V_{c}^{\#} \tag{2-30}$$

Combination of equations (2-28) and (2-29) yields:

$$\Delta V_{ab}{}^{*} + \Delta V_{bc}{}^{*} = \Delta V_{a}{}^{\#} - \Delta V_{c}{}^{\#} \qquad (2\text{-}31)$$

which is the difference between the partial monomer activation volumes of the monomers a and c.
Consequently:

$$\Delta V_{ac}{}^{*} = \Delta V_{ab}{}^{*} + \Delta V_{bc}{}^{*} \qquad (2\text{-}32)$$

Conclusion:

Under condition that $d\ln(r_a{}^{*}\ r_b)/dp = 0$ holds universally, knowledge of the pressure dependence of the copolymerizations of monomer b with monomers a and c makes it possible to calculate the pressure dependence of the copolymerization of monomer a with c .

It is possible to set up a scheme of correlation, allowing predictions for the pressure dependence of the r-values of a series of systems. The scheme is based on the difference between the partial monomer activation volume of one monomer and the partial monomer activation volumes of a series of other monomers.

If the activation volume cannot be described as the sum of independent partial volumes, it can be expected that the scheme *at least* allows estimation of pressure influences.

In Chapter 5, the results of the present investigation will be viewed in the light of this hypothesis.

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CHAPTER 3

METHODS OF DETERMINING MONOMER REACTIVITY RATIOS

In the literature on the subject several methods are described for the determination of monomer reactivity ratios (*r*-values).
Roughly the methods can be divided into two groups.

In the first group every kinetic run yields *two* data pairs belonging to the start and the end of the copolymerization reaction. These data pairs are connected by the differential versions of the copolymerization equation (2-1 or 2-2). Data resulting from a series of runs can be combined into a series of differential equations containing the substituted data pairs. The *r*-values can be resolved by a graphical method: the "intersection method".

In the second group *many* data pairs are gathered during every kinetic run. A statistical least-squares method is applied to the data pairs and the integrated version of the copolymerization equation (2-3). By doing this, each run produces a nearly straight curve which correlates the two *r*-values. Curves resulting from a series of runs can be combined by the "intersection method", thus yielding the desired *r*-values. German (ref. 1) applied this method for the first time to the results of sequential measurement of the monomer concentrations and called it: Feed Compositional Analysis Method-A (F.C.A. method-A).
However, all data, gathered during this series of runs, can be treated simultaneously by a least-squares method that leads directly to the desired *r*-values.
German (ref. 1) also applied this type of evaluation and called it: F.C.A. method-B.

Moreover, comparison of the least-squares sums of the deviations between model and experiment, respectively determined by the methods -A and -B, and consideration of the contribution of every run to this sum of squares enabled German to judge the correctness of the chemical kinetic model underlying the copolymerization equations.

In the next sections the mathematical basis and principles for evaluation will be discussed. The integral versions of the copolymerization equation differ in their limits from those of German because of the experimental procedure used for copolymerization under high pressure. This procedure, the "sandwich" method, is described in Chapter 5.
In Appendix I a statistically based test will be described that makes it possible to judge the competency of a model function to describe experimental data.

3.1 PRINCIPLES OF THE EVALUATION OF THE *r*-VALUES

For a certain interval of relative conversion $0 - F_b$ the integrated form of the copolymerization equation (2-3) may be rearranged, yielding:

$$F_b - 100 * \left\{ 1 - \left(\frac{q}{q_s}\right)^{-x_2-1} * \left(\frac{x_2 q - x_1}{x_2 q_s - x_2}\right)^{x_1+x_2+1} \right\} = 0 \qquad (3\text{-}1)$$

in which $F_b = 100 * \left\{ 1 - f_b/(f_b)_s \right\}$,
$f_b = n_b/(n_b)_o$,
$(f_b)_s = (n_b)_s/(n_b)_o$,
$x_1 = 1/(r_a-1)$,
$x_2 = 1/(r_b-1)$,
$q_s = q(F_b=0)$,
the subscript zero denotes initial conditions,
the subscript *s* denotes arbitrary start conditions.

During all calculations, precautions will be taken to avoid infeasible solutions of this equation by the requirements listed in 2.1.1. In addition, the possible r-values will be confined to the relevant, i.e. positive, values. The given model description can be formulated briefly as follows:

$$F_b - F(r_a, r_b, q_s, q) = 0$$

In Chapter 4 it will be shown that in this investigation the experimental data, after preliminary calculations, are available as a series of values $q_i = (n_a/n_b)_i$, describing the monomer feed composition at the corresponding relative degrees of conversion F_b .

3.1.1 F.C.A. METHOD-A

Each kinetic series, producing g data pairs $\left(q_i, (F_b)_i\right)$, yields g conversion intervals $0 - (F_b)_i$ and consequently g equations ΔF_i :

$$\Delta F_i\left(r_a, r_b, q_s, q_i, (F_b)_i\right) = (F_b)_i - F(r_a, r_b, q_s, q_i) \tag{3-2}$$

in which $i = 1, \ldots, g$,
g = the number of data pairs resulting from one experiment $\geqslant 2$.

ΔF_i represents the difference between the measured relative conversion $(F_b)_i$ and the corresponding relative conversion calculated by the model function. The latter is still an implicit function of the unknown parameters:

- r_a and r_b, which are constants for all experiments if the model is adequate,

- q_s, which is characteristic of one distinct experiment and will generally not be much different from the measured value $q(F_b = 0)$.

Generally each experiment supplies a large number ($g >> 2$) of experimental data. Owing to the experimental error, generally $\Delta F_i \neq 0$ ($i=1,\ldots,g$) for any r_a, r_b and q_s combination. Therefore theoretically one single kinetic experiment gives sufficient information to determine the least-squares estimates for $\hat{r}_a$, $\hat{r}_b$ and $\hat{q}_s$ by selecting those values of r_a, r_b and q_s that minimize:

$$\sum_{i=1}^{g} \Delta F_i^2 \left(r_a,\ r_b,\ q_s,\ q_i,\ (F_b)_i\right)$$

leading to:

$$P = P\ (\hat{r}_a,\ \hat{r}_b,\ \hat{q}_s) = \sum_{i=1}^{g} \Delta F_i^2 \left(\hat{r}_a,\ \hat{r}_b,\ \hat{q}_s,\ q_i,\ (F_b)_i\right)$$

P = the residual sum of the squares of the deviations in F_b ;

$\hat{r}_a$, $\hat{r}_b$ and $\hat{q}_s$ are the estimates of r_a, r_b and q_s, i.e. those parameters that minimize $\sum_{i=1}^{g} \Delta F_i^2$.

Earlier, however, explorative investigations have shown that from the data of one single kinetic experiment no estimates $\hat{r}_a$ and $\hat{r}_b$ can be found for r_a and r_b, as the minimum of the function $\sum_{i=1}^{g} \Delta F_i^2 = P\ (r_a,\ r_b,\ q_s)$ is indeterminate.

Instead of a single *point* in the $r_a - r_b - q_s$ space a *line* is found which comes up to the condition that

$\sum_{i=1}^{g} \Delta F_i^2$ must be minimal. The correlation between $\hat{r}_a$ and $\hat{r}_b$, as gathered from one single experiment, is evidently caused by the existence of an experimental error combined with the fact that within one experiment q changes only to a relatively small extent.

Any kinetic series affords such a line, which is approximately parallel to the $r_a - r_b$ plane with practically the same value of q_s.

In case an experiment supplies only two data pairs ($g = 2$), the two equations with the unknown parameters r_a, r_b and q_s can only be resolved by substituting $\Delta F_i = 0$ and $q_s = q_1$ thus yielding a relation between $\hat{r}_a$ and $\hat{r}_b$. This case is an extreme example of the correlation between r_a and r_b, as they are 100% correlated. For an infinitesimal change of q, the experiment degenerates into testing the differential version (2-2). In that case a linear relation between $\hat{r}_a$ and $\hat{r}_b$ holds.

The use of the differential versions (2-1) and (2-2) for a finite change of q causes systematic deviations in the relation between $\hat{r}_a$ and $\hat{r}_b$.

3.1.2 INTERSECTION METHOD ACCORDING TO F.C.A. METHOD-A

In order to determine the relations between $\hat{r}_a$ and $\hat{r}_b$ mentioned (cf. 3.1.1), the experimental data $\left(q_i, (F_b)_i\right)$ of one kinetic experiment are substituted into equation (3-3). Thereupon, in the region where the $\hat{r}_a$-value is to be expected, $\hat{r}_a$ is successively assigned a number of values and

$$P = \sum_{i=1}^{g} \Delta F_i^2 \left(r_a,\ r_b,\ q_s,\ q_i,\ (F_b)_i\right)$$

is minimized with respect to r_b and q_s. Thus a relation between $\hat{r}_a$ and $\hat{r}_b$ is determined for the kinetic experiment in question.
This procedure is repeated for all kinetic series.

F.C.A. method-A is continued as follows (ref. 1):

- For all kinetic series, which are different in initial monomer feed ratio, the points with co-ordinates $(\hat{r}_a, \hat{r}_b)$ are plotted in a graph of $\hat{r}_a$ versus $\hat{r}_b$.
- Since the $\hat{r}_a - \hat{r}_b$ relations appear to be practically straight lines in the region of interest, linear regression is applied to determine these lines for each experiment.
- The centre of gravity of the area defined by the significant intersection points is taken as the best fitting pair of r-values for the set of experiments concerned.
- From the dimensions of the area of intersection points, the errors in the r-values can be estimated.

3.1.3 F.C.A. METHOD-B

The information resulting from all kinetic experiments $(k=1,\ldots,n)$ may be combined to determine the least-squares estimates for r_a, r_b as well as the initial molar feed ratios q_{sk} for all kinetic series simultaneously. This can be done by minimizing:

$$P = \sum_{k=1}^{n} P_k = \sum_{k=1}^{n} \sum_{i=1}^{g_k} \Delta F_{ik}^{2} \left(r_a, r_b, q_{sk}, q_{ik}, (F_b)_{ik}\right)$$

with respect to r_a, r_b and q_{sk} $(k=1,\ldots,n;\ n$ = number of experiments). This minimization procedure immediately leads to the least-squares estimates for r_a, r_b and q_{sk} and the value of the residual sum of squares P.

3.1.4 COMPUTER PROGRAMS FOR THE EVALUATION OF THE EXPERIMENTAL DATA

For the solution of the non-linear least-squares method, a computer program in Algol-60 has been written. This program has been derived from a general procedure, reported by Lootsma (ref. 2), for solving constrained or unconstrained minimization problems.

Computation of the error in $\hat{r}_a$ and $\hat{r}_b$

By means of an Algol procedure described by Linssen (ref. 3) the standard deviations can be calculated of a set of parameters, estimated with least-squares methods. The principles of this error evaluation are discussed by Behnken (ref. 4) and German (ref. 1).

By means of an Algol procedure described by Braakman (ref. 5) the joint confidence limits of a *pair* of parameters, estimated with least-squares methods can be calculated. The joint confidence limits are to be given preference over the perpendicular confidence intervals (standard deviations), since only the former convey the message of which *pairs* of r_a, r_b values are consistent with the input data.

The joint confidence limits (or confidence regions) are elliptical contours in which the correct pair of r-values is supposed to lie at a stated probability level. Practically identical methods of calculating confidence regions are reported by Behnken (ref. 4) and Tidwell and Mortimer (ref. 6).

3.2 STATISTIC TESTING OF THE FITTING BETWEEN MODEL FUNCTION AND EXPERIMENTAL DATA

A number of experiments has been performed. The experimental outcomes are assumed to follow the same model function. This function contains parameters with unknown values.

For each experiment separately these parameters can be estimated by the least-squares method. Summation of the residual sums of the squares yields the "summed sums of the squares".

Some of the unknown parameters may be assumed to be equal for all experiments and can be estimated. It is obvious that this estimation results in an "overall residual sum of the squares" which exceeds the "summed sums of the squares".

The ratio of this difference to the "summed sums of the squares" follows approximately, under some restrictions (cf. Appendix I), a known distribution. This makes significance-testing possible.

A high value of this ratio, violates the assumption that the parameters mentioned are equal for all experiments.

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CHAPTER 4

RELATION BETWEEN THE COMPOSITION OF THE REACTION MIXTURE AND THE PRIMARY EXPERIMENTAL DATA

In Chapter 5 an experimental procedure will be described, based on quantitative gas chromatography. As a result of any sampling from the reactor three peaks arise, representing the concentrations of the two monomers and the solvent.

In behalf of the computation of the monomer reactivity ratios (*r*-values), the monomer feed ratios and the relative degrees of conversion have to be calculated from sample and reference peak areas. These calculations are complicated by contraction of the reaction volume due to copolymerization and by precipitation of copolymer in the sampling chamber, thus causing changes in the volume injected by the sampling valve. However, generally applicable relations can be derived, making use of reference peak areas of the pure monomers and using the solvent as an internal standard.

An improved method of determining the reference peak areas will be described, using a piston type of pressurizer to inject liquid samples at the same pressure level as gaseous samples.

Systematic errors nevertheless are present and in Appendix II the sources of these errors will be analyzed, approximating models will be given and the transmission of this kind of errors into the *r*-values will be simulated.

Sources of statistic errors have been discussed and their importance has been approximated by German (ref. 1).

4.1 CALCULATION OF THE PRIMARY EXPERIMENTAL DATA

4.1.1 CALCULATION OF THE REACTION TIME BASIS

The reaction time basis is derived from the moment the summit of a peak is detected by substraction of the relevant retention time.

4.1.2 ESTIMATION OF THE MOMENT OF PRESSURE CHANGE

In behalf of the "sandwich" method described in Chapter 5, the moment of pressure change has to be estimated from time-pressure observations. This point of time has been determined by interpolating the moment, at which 50% of the total pressure change has been accomplished.

4.1.3 CALCULATION OF MONOMER FEED RATIO AND RELATIVE CONVERSION FROM PEAK AREAS DETERMINED BY GAS CHROMATOGRAPHIC ANALYSIS

The symbols used in the derivation are:

c = molar concentration	a = monomer a
n = number of moles	b = monomer b
f = relative amount of feed	i = inert solvent
A = peak area	s = sample
V = volume	r = reference

The number of moles monomer "a" in the reaction chamber is determined by:

$$n_a = \frac{A_{as}}{A_{ar}} * n_{ar} * \frac{V}{V_s} \qquad (4\text{-}1a)$$

in which n_a = number of moles "a" in the reaction chamber,

n_{ar} = number of moles "a" injected by the reference disk valve,

A_{as} = peak area of "a" from a sample injection,

A_{ar} = peak area of "a" from a reference injection,

$\frac{V}{V_s}$ = ratio of the volume of the reaction chamber and the volume injected by the sampling valve.

Similarly:

$$n_b = \frac{A_{bs}}{A_{br}} * n_{br} * \frac{V}{V_s} \tag{4-1b}$$

$$n_i = \frac{A_{is}}{A_{ir}} * n_{ir} * \frac{V}{V_s} \tag{4-1c}$$

The number of moles of pure "a" injected by the reference disk valve is governed by:

$$n_{ar} = c_{ar} * V_r \tag{4-2}$$

in which c_{ar} = concentration of pure "a" under reference conditions,

V_r = volume injected by the reference disk valve (at fixed temperature and pressure this volume is constant),

n_{ar} = number of moles pure "a" injected by the reference valve.

Similar relations hold for "b" and "i".

During a kinetic run the number of moles inert solvent "i" in the reaction chamber is constant. Therefore:

$$\frac{n_i}{V_{io}} = \frac{n_{ir}}{V_r} = c_{ir} \tag{4-3}$$

in which n_i = number of moles "i" in the reaction chamber,
V_{io} = volume of pure "i" introduced into the reactor under reference conditions,
n_{ir} = number of moles pure "i" injected by the reference disk valve,
V_r = volume injected by the reference disk valve,
c_{ir} = concentration of pure "i".

Substitution of equation (4-3) into (4-1c) yields after rearranging:

$$\frac{V}{V_s} = \frac{A_{ir}}{A_{is}} * \frac{V_{io}}{V_r} \tag{4-4}$$

This equation describes the volume ratio $\frac{V}{V_s}$ with the aid of the internal standard "i".

Combination of equations (4-1a), (4-2) and (4-4) yields:

$$n_a = \frac{A_{as}}{A_{is}} * \frac{A_{ir}}{A_{ar}} * V_{io} * c_{ar} \tag{4-5}$$

In the same way:

$$n_b = \frac{A_{bs}}{A_{is}} * \frac{A_{ir}}{A_{br}} * V_{io} * c_{br} \tag{4-6}$$

From equations (4-5a) and (4-5b) it follows that:

$$q = \frac{n_a}{n_b} = \frac{A_{as}}{A_{bs}} * K_{ref} \tag{4-7}$$

in which $$K_{ref} = \frac{A_{br} * c_{ar}}{A_{ar} * c_{br}} \tag{4-8}$$

and $$f_b = \frac{n_b}{n_{bo}} = \frac{A_{bs}}{A_{is}} * \frac{A_{iso}}{A_{bso}} \tag{4-9}$$

in which f_b = relative amount of feed based on b;
the subscript zero denotes initial conditions.

K_{ref} is calculated from:
- peak areas supplied by reference injections,
- density of pure monomer at the relevant conditions supplied by literature (ref. 2).

Relative degree of conversion between the moments i and j can be calculated by:

$$F_b = 100 * \left\{ 1 - (f_b)_i / (f_b)_j \right\} \tag{4-10}$$

For equations (4-7) to (4-10) the estimations of the errors given by German (ref. 1) hold.

4.1.4 DETERMINATION OF THE REFERENCE PEAK AREAS

It appears from the derivation of equation (4-8) that the calculation of K_{ref} requires a constant sample size during the reference injections. German (ref. 1) recognized the pressure dependence of the sample size and approximated its pressure dependence. Unfortunately it was found during this research, that the sample size is also dependent of the time interval that the sample chamber has been pressurized and depressurized. Therefore gaseous and liquid samples must be injected at the same pressure level, the sample chamber must be preconditioned under reference conditions, and depressurizing of the sample chamber by injecting, may only take place during a fixed time-interval.

The requirements listed above have been met by the reference system used during this research. The scheme of the system is shown in Fig. 4-1.
The main components are:

- a piston type of pressurizer in behalf of liquid reference samples (cf. Fig. 4-2),

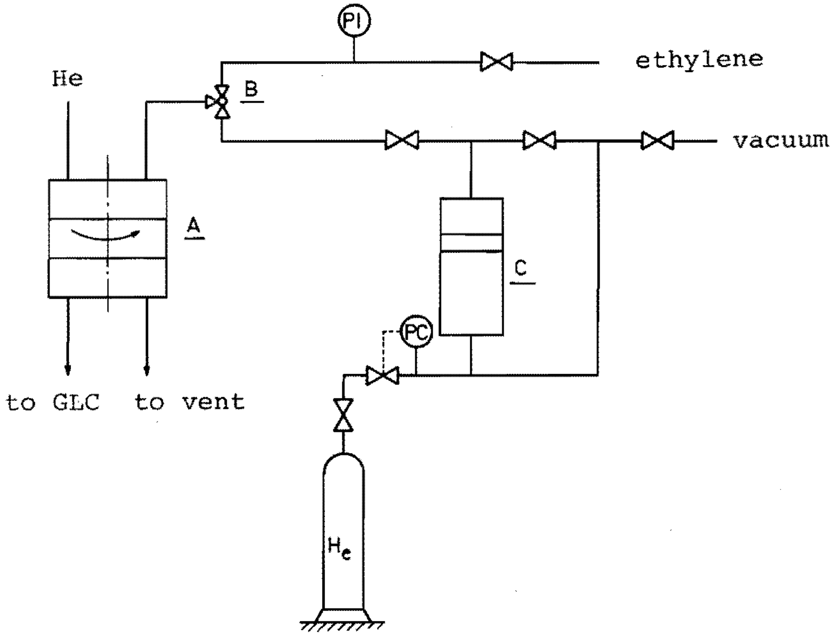
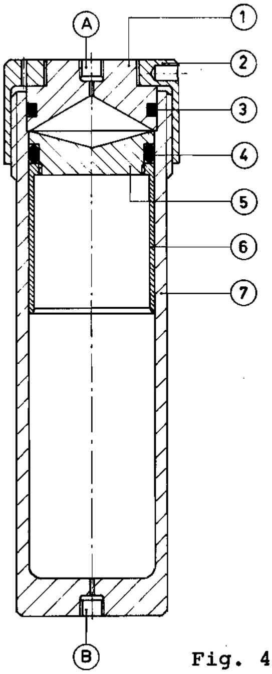


Fig. 4-1 Simplified scheme of the reference equipment;

A = disk valve;
B = ball valve;
C = piston type of pressurizer.



A	sample outlet;
B	pressurizing connection;
1	plug;
2	overhead nut;
3 and 4	"O"-ring Viton;
5	piston;
6	removable piston guide;
7	cylinder.

Fig. 4-2 Piston type of pressurizer

- a vacuum system to degas the liquid reference sample inside the pressurizer,
- an adjustable constant-pressure He supply unit to pressurize the liquid reference sample,
- a time-interval switch, actuating the disk valve by means of a pneumatic actuator, that permits the sample chamber to stay in the low-pressure carrier gas stream of the gas chromatograph for a fixed time interval,
- a ball valve to select the gaseous or the liquid sample supply stream,
- a precise absolute-pressure gauge to adjust the pressure of the gaseous samples,
- an air bath in which the valve is placed, is temperature-controlled by a proportional controller with adjustable derivative and integral action. Pt 100 resistance temperature sensors inside the valve body are used.

The determination of A_{er} and A_{vr}

First ethylene gas is injected until approximately 25 peak areas are registered of a constant level. Then vinylacetate is injected until approximately 25 peak areas of a constant level are registered. Finally again ethylene gas is injected until about 25 peak areas of a constant level are obtained. The mean of this group of ethylene peaks may not deviate within the standard deviation from the mean of the first group of ethylene peaks. When this condition is met, it is likely that the volume of the sample and other conditions during the experiment have not changed. Then K_{ref} may be calculated, using c_{er} and c_{vr} taken from literature (ref. 2) under the relevant conditions. In this research the standard deviations of the A_{er} peak areas have been estimated to be $<.1\%$ and those of A_{vr} to be $<.2\%$.

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CHAPTER 5

DETERMINATION OF THE EFFECT OF PRESSURE ON THE MONOMER REACTIVITY RATIOS

5.1 INTRODUCTION

In Chapter 3 methods of determining *r*-values by frequent analysis of the monomer feed composition have been described.

German (ref. 1) describes an experimental quantitative gas chromatographic method, the "sequential sampling" method, which

- is applicable to pressures up to 50 kg/cm^2 and temperatures up to 100°C,
- affords the possibility of the determination of the number of moles (except for a constant factor) of both monomers in the reactor during copolymerization experiments up to high conversions (40%),
- leads to the accessibility of the characteristic variables, viz. the monomer feed ratio and the degree of conversion (cf. Chapter 4),
- offers the possibility of generating curves of monomer feed ratio versus reaction-time and/or conversion by non-linear least-squares methods, leading to the least-squares estimates for the *r*-values (cf. Chapter 3),
- is particularly favourable when gaseous monomers are involved.

To extend the applicability of the "sequential sampling" method (ref. 1) to high pressures, a high pressure sampling system based on line-sealing has been developed and tested (cf. Appendix III). Tests showed that the proto-

type might be applied up to several hundreds kg/cm^2 for sampling a gas chromatograph from a high-pressure vessel. However, accuracy was affected by an underdeveloped evaporation chamber, causing noticeable diffusion controlled evaporation of monomers and solvent from copolymer precipitated (cf. Appendix II). Because of time limits and shortness of man-power resulting from the retrenchment policy further development of this promising generally applicable method went beyond the scope of this thesis.
Since in its stage of development, this device would provide considerable systematic deviations of the results, this technique has been abandoned in the present study.

In order to determine the *effect* of pressure on the r-values *without* the help of a high-pressure sampling method, the "sandwich" method has been developed, tested and applied. Here low-pressure r-values and high-pressure r-values have been estimated from the *same* population of experimental kinetic data, gathered at *low* pressure. As a consequence low-pressure sampling methods can be used. Except for some minor modifications, the "sequential sampling" method described by German is followed.

5.2 SET UP OF THE "SANDWICH" EXPERIMENTS

During a kinetic experiment, pressure is raised for a certain time-interval in such a way that: pressurizing and depressurizing time << reaction time at high pressure. Thus the experiment is split up into three stages:

- an initial stage at a low-pressure level,
- an intermediate stage at a high-pressure level,
- a final stage at a pressure level identical with that of the initial stage.

Each stage contributes to the conversion of the monomers. This implies identity of the monomer feed compositions:

- at the end of the initial and the beginning of the intermediate stages,
- at the end of the intermediate and the beginning of the final stages.

The monomer feed composition is frequently measured throughout the initial and final stages with the aid of the "sequential sampling" method (ref. 1). However, during the intermediate stages no samples are taken. The sampling valve is isolated from the reactor during this stage and thus guarded against damage by excessive pressure.

These measurements produce sets of data and curves for the initial and final stages. These results make it possible to determine accurately the monomer feed composition at the beginning and end of the intermediate stage. A series of "sandwich" runs results in the same number of sets of data.

In Chapter 4 it has been shown in which way the numbers of moles of the monomers in the reactor can be derived, using the fact that the number of moles inert solvent in the reactor is *constant* during a kinetic experiment.

In order to compensate for pressure changes due to contraction and sampling, the volume of the reaction chamber has been made variable by application of bellows.

5.3 ESTIMATION OF r-VALUES FROM THE DATA COLLECTED DURING "SANDWICH" EXPERIMENTS

By least-squares methods applied to the integrated copolymerization equation (2-3) and the equation of monomer feed ratio and time (2-16), conversion and monomer feed ratio at the beginning and end of the intermediate stage can be extrapolated from three series of low-pressure data:

monomer feed ratio - conversion,
monomer feed ratio - reaction time,
pressure - reaction time.

The estimation method will be described and is illustrated by Fig. 5-1.

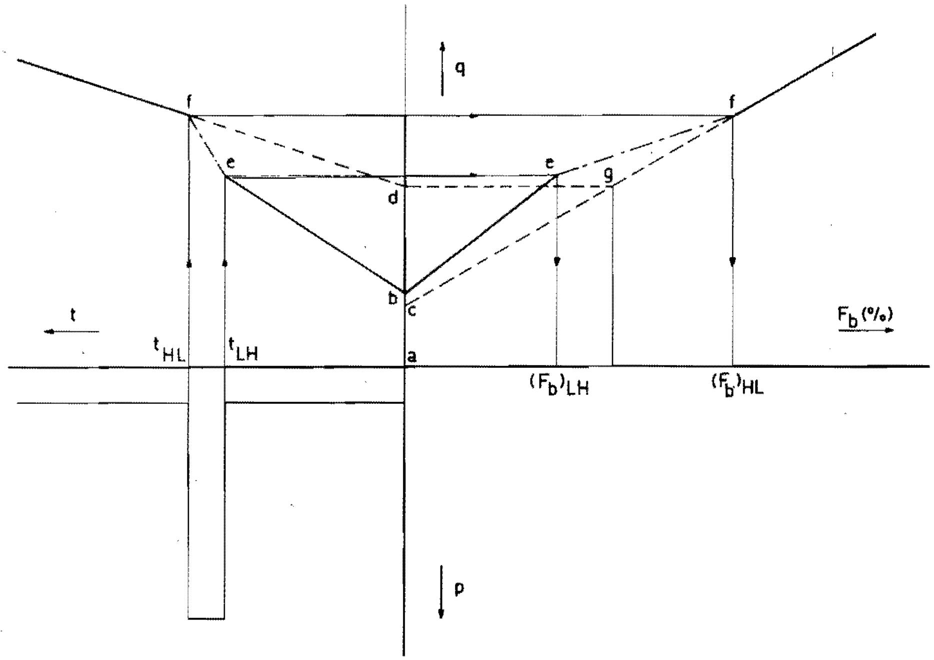

Fig. 5-1 Scheme of "sandwich" method

t = time basis.
$F_b = 100 * \{1 - f_b/(f_b)_s\}$ conversion basis.

Explanation of the important points a, b, c, d, e and g in the plot:

a $t = t_s$; $F_b = 0$: start of the conversion and time basis;
b $\hat{q}_s(t = t_s) = \hat{q}_s(F_b = 0)$: *real* initial monomer feed ratio of the initial stage;
c and d $\hat{q}(t = t_s) \neq \hat{q}(F_b = 0)$: *virtual* initial monomer feed ratios of the final stage;

b and c $\hat{q}_s(F_b=0)_{\text{initial stage}} \neq \hat{q}(F_b=0)_{\text{final stage}}$;
b and d $\hat{q}_s(t=t_s)_{\text{initial stage}} \neq \hat{q}(t=t_s)_{\text{final stage}}$;
e $(t, \hat{q}, \hat{F}_b)_{LH}$: co-ordinate of the beginning of the intermediate and the end of the initial stage;
f $(t, \hat{q}, \hat{F}_b)_{HL}$: co-ordinate of the end of the intermediate and the beginning of the final stage;
g see 5.3.1.

5.3.1 COMMON BASES OF THE DIFFERENT STAGES

For reasons of calculation the three stages of a "sandwich" experiment are joined by two bases, common for the three stages of one experiment:

- the time basis t,
- the relative conversion basis F_b.

The moment that the first sample is taken, the bases are started as follows:

- $t = t_s$,
- $F_b = 0$, because $(f_b)_s = f_b\ (t = t_s)$ by definition (cf. 3.1).

This approach implies that (cf. Fig. 5-1):

- the three stages of a "sandwich" experiment may be considered independent during calculations,
- in the initial stage $\hat{q}_s(t = t_s) = \hat{q}_s(F_b = 0)$,
- in the final stage, the *virtual* value of $\hat{q}(t = t_s)$, given by equation (2-16) and the *virtual* value $\hat{q}(F_b = 0)$, given by equation (2-3), are different. They do not coincide, as for the final stage, $t = t_s$ and $F_b = 0$ are arbitrary starts of the time and relative conversion scale. So, $\hat{q}(t = t_s)$ must belong to a value $F_b \neq 0$, which can be found by searching the value for F_b in the $q - F_b$ plot (cf.

Fig. 5-1: point g), that corresponds with the co-ordinate $q(t = t_s)$,

- the *real* value $\hat{q}_s(F_b = 0)$, in the initial stage, is not equal to the *virtual* value $\hat{q}(F_b = 0)$, in the final stage (cf. points b and c in Fig. 5-1), because of the effect of pressure on the r-values during the intermediate stage (cf. equation (2-3)),
- the *real* value $\hat{q}_s(t = t_s)$, in the initial stage, is not equal to the *virtual* value $\hat{q}(t = t_s)$, in the final stage (cf. points b and d in Fig. 5-1), because of the effect of pressure on propagation, termination and initiation rate constants during the intermediate stage (cf. equation (2-16)).

5.3.2 ESTIMATION OF THE r-VALUES AND $\hat{q}_{sk}$ DURING THE LOW-PRESSURE STAGES

n "sandwich" experiments different in initial monomer feed ratio, cover $2n$ independent low-pressure experiments. These experiments yield $\sum_{k=1}^{2n} g_k$ co-ordinates, from which $\hat{r}_a$, $\hat{r}_b$ and $\hat{q}_{sk}$ can be estimated with the aid of F.C.A. methods-A and/or -B (cf. 3.1.1 and 3.1.3 : $g >> 2$).

5.3.3 PRINCIPLES OF THE EVALUATION OF THE r-VALUES DURING THE INTERMEDIATE STAGES

The estimation of the r-values during the intermediate stages, at least requires knowledge of the monomer feed composition at the beginning and end of the intermediate stages of a set of "sandwich" experiments (cf. 3.1 : $g = 2$). The next section will show how these data can be estimated.

5.3.3.1 Estimation of the monomer feed composition at the beginning and end of the intermediate stages

For a certain time interval $t_s - t$ the equation of monomer feed ratio and time (2-16) may be rearranged, yielding:

$$q=R*\frac{1+\arcsin\left\{S*\left(\exp\left(-\tfrac{1}{2}*k_d*(t-t_s)\right)-1\right)+\sin^{-1}\left(\frac{q_s-R}{q_s+R}\right)\right\}^{-1}}{1-\arcsin\left\{S*\left(\exp\left(-\tfrac{1}{2}*k_d*(t-t_s)\right)-1\right)+\sin^{-1}\left(\frac{q_s-R}{q_s+R}\right)\right\}^{-1}} \qquad (5\text{-}1)$$

at which $t_s =$ the moment which the time basis is initiated,

$q_s = q(t_s)$,

$S = (I_o)^{\frac{1}{2}}*T$,

$I_o = I(t_s)$,

$T = (r_a - 1) * \left(R * \dfrac{\alpha * k_{ab} * k_{ba}}{k_{tab} * k_d}\right)^{\frac{1}{2}}$,

$R = (1-r_a)/(r_b-1)$.

Parameter S is unknown and different for all low pressure stages of these experiments, because:

- I_o is different for all stages and experimentally inaccessible,
- T is unknown and the same for all low-pressure stages of the "sandwich" experiments.

Kinetic constant k_d has been reported by literature (ref. 2).

Estimation of the parameters in equation (5-1)

The model description given in equation (5-1) can be formulated briefly as:

$$q - Q\ (S,\ q_s,\ t_s,\ t) = 0$$

The parameters S and q_s are characteristic of one distinct stage of a set of "sandwich" experiments.

Each low-pressure stage, producing g data pairs, ($g \geqslant 2$) yields g conversion intervals $t_s - t_i$ and consequently g equations ΔQ_i (cf. 3.1.1).

$$\Delta Q_i\ (S,\ q_s,\ t_s,\ t_i) = q_i - Q\ (S,\ q_s,\ t_s,\ t_i)$$

One kinetic stage gives sufficient information to determine the least-squares estimates for S and q_s that minimize

$$P = \sum_{i=1}^{g} P_i = \sum_{i=1}^{g} \Delta Q_i^{\ 2}\ (\hat{S},\ \hat{q}_s,\ t_s,\ t_i)$$

P = residual sum of the squares of the deviations in q, $\hat{S}$ and $\hat{q}_s$ are the estimates for S and q_s, i.e. those parameters that minimize $\sum_{i=1}^{g} P_i$.

The estimation of the monomer feed composition at the beginning and end of the intermediate stages

At the moment that pressure is raised (= t_{LH}) and at the moment pressure is lowered (= t_{HL}), the intermediate stage is bounded by low-pressure stages:

- the initial stage characterized by the estimates $(\hat{S})_{\mathrm{in}}$ and $(\hat{q}_s)_{\mathrm{in}}$,
- the final stage characterized by the estimates $(\hat{S})_{\mathrm{f}}$ and $(\hat{q}_s)_{\mathrm{f}}$.

The monomer feed ratio at the beginning of the intermediate stage $\hat{q}_{\mathrm{LH}}$ is estimated by substitution of t_s, t_{LH} and $(\hat{S},\ \hat{q}_s)_{\mathrm{in}}$ into the (q-t) relation (5-1). The corresponding relative conversion $(\hat{F}_{\mathrm{b}})_{\mathrm{LH}}$ can be estimated by substitution of $(\hat{q}_s)_{in}$, $\hat{q}_{LH}$ and $(\hat{r}_a, \hat{r}_b)_{low\text{-}pressure}$ into the $(q\text{-}F_b)$ relation (3-1).

The monomer feed ratio at the end of the intermediate stage $\hat{q}_{HL}$ is estimated by substitution of t_s, t_{HL} and $(\hat{S},\hat{q}_s)_f$ into the $(q\text{-}t)$ relation (5-1). The corresponding relative conversion $(\hat{F}_b)_{HL}$ can be estimated by substitution of $(\hat{q}_s)_f$, $\hat{q}_{HL}$ and $(\hat{r}_a, \hat{r}_b)_{low\ pressure}$ into $(q\text{-}F_b)$ relation (3-1).

5.3.3.2 Estimation of the r-values during the intermediate stages

From n sandwich experiments n pairs of co-ordinates can be estimated (cf. 5.3.3.1):

$$(t_j,\ \hat{q}_j,\ (\hat{F}_b)_j)_{LH}\ ,$$
$$(t_j,\ \hat{q}_j,\ (\hat{F}_b)_j)_{HL}\ ,$$
$$1 \leqslant j \leqslant n\ .$$

The relative conversion during the intermediate stage can be calculated by:

$$(F_b)_j = 100 * \left\{ 1 - \frac{100 - (F_b)_{jLH}}{100 - (F_b)_{jHL}} \right\} \%$$

From $\hat{q}_{jLH}$, $\hat{q}_{jHL}$ and $(F_b)_j$, the r-values can be estimated using F.C.A. methods-A and -B (cf. 3.1.1 and 3.1.3 with $g = 2$).

5.4 APPARATUS

A block diagram of the high-pressure reaction system and its main components is shown in Fig. 5-2.

The gas chromatographic system that has been used, satisfies the requirements given by German (ref. 1).

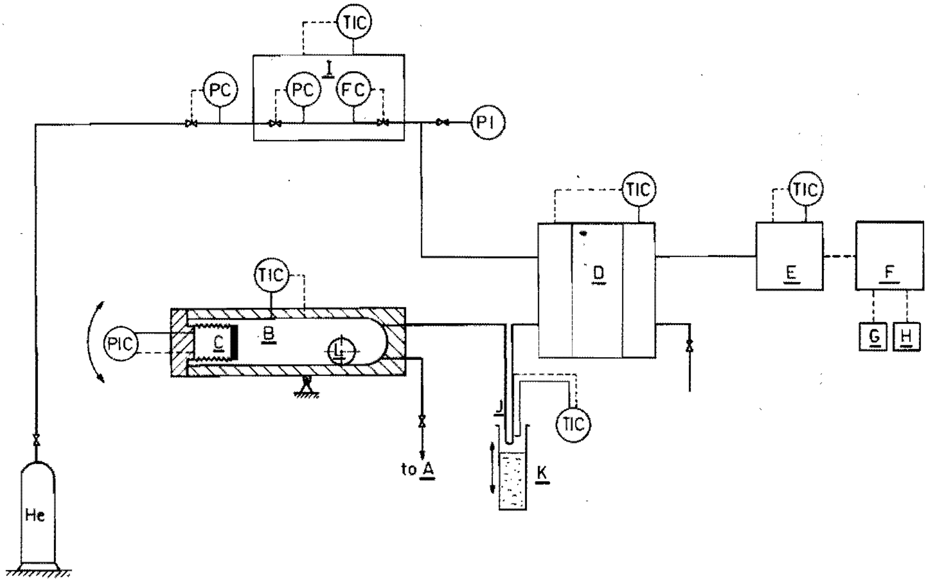

Fig. 5-2 Simplified scheme of the integral equipment

A = filling and draining connection;
B = reaction chamber;
C = compartment for pressure control;
D = sampling device;
E = gas chromatograph;
F = electronic integrator;
G = recorder;
H = digital printer and puncher;
I = mass flow controller unit;
J = cryogenic capillary hairpin valve;
K = Dewar vessel filled with liquid N_2;
L = Teflon coated lead ball.

5.4.1 THE HIGH-PRESSURE REACTOR

The high-pressure experiments described in this thesis have been carried out in a modified version of an Autoclave Engineers autoclave type no 261575 Z. It is manufactured from stainless steel A 286. At 62°C the maximum working pressure is 2500 kg/cm^2. It is provided with an external cylindrical jacket through which water is circulated by a thermostat.

The vessel comes up to the requirement of a closed system with one (liquid) phase. This is met by a Teflon bellows that separates the reaction chamber and the compartment for pressure control (cf. Fig. 5-3). Pressure is controlled by the amount of *iso*-propylalcohol pressed into the compartment for pressure control.

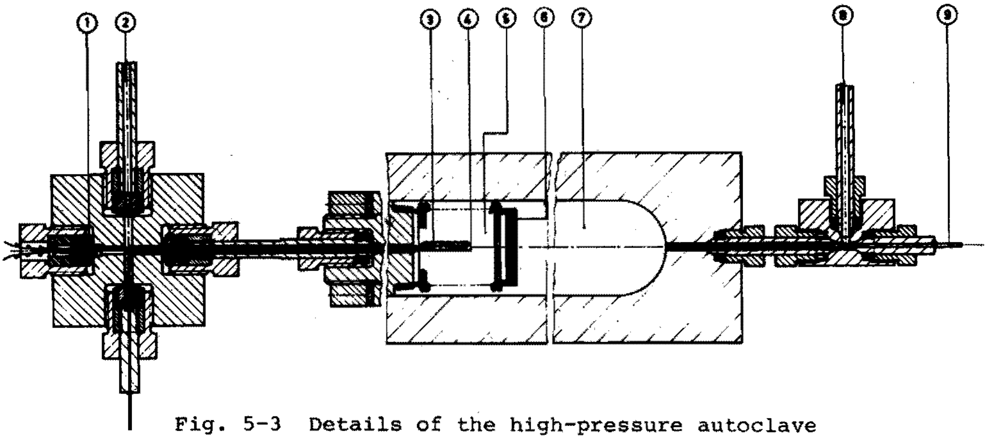

Fig. 5-3 Details of the high-pressure autoclave
1 = bushing insulator;
2 = pressurizing tube;
3 = PT 100 resistance thermometer;
4 = thermo-couple;
5 = compartment for pressure control;
6 = Teflon bellows;
7 = reaction chamber;
8 = filling and draining tube;
9 = capillary sampling tube.

The reactor is rocked and the contents of the reaction chamber are stirred by the movement of the Teflon coated lead ball inside.

Reaction temperature is measured by means of a PT 100 resistance thermometer and a co-axial iron-constantan thermocouple. The pressure-tight bushing insulator connected with the PT 100 has specially been developed for this application.

5.4.2 PERIPHERY OF THE HIGH-PRESSURE REACTOR

The kinetic experiments carried out in the high-pressure reactor need an accurate and fast responding control of temperature and pressure inside the vessel.

The temperature control

A fast response of the reactor contents to the temperature of the water flowing through the jacket is hindered by the thick stainless steel reactor wall.
The water temperature should respond rapidly to temperature variations inside the reactor, without overshoot.

This is achieved by:

- Mixing of a cold and a hot water flow by a control valve. The mixture is pumped through the jacket.
- Three PT 100 resistance thermometers: one in the valve outlet, another in the jacket inlet and a third inside the compartment for pressure control.
- Linking the PT 100 thermometers into a Wheatstone bridge.

The signal from the bridge is fed into a servo amplifier

that adjusts the position of the control valve by means of a servo motor.
The system has been optimized by adjustment of the amplifier gain and variable resistors in the Wheatstone bridge. An accuracy of ± .2°C *) at 62°C is achieved in the reaction mixture.

The pressure control

A fast responding and accurate pressure control system has been assembled from the following components:

- A high-pressure diaphragm pump with remote controllable piston stroke, type Lewa 5V-H.
- 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.
- A pneumatically actuated Annin Model 5060 "Wee Willie" Domotor valve.

Pressure is transmitted by *iso*-propylalcohol. The system is optimized by adjusting the pump piston stroke and the proportional and integral action of the controller. The accuracy obtained is ± .5 kg/cm^2 *) at 35 kg/cm^2 and ± 10 kg/cm^2 *) at 600 kg/cm^2.

5.4.3 THE SAMPLING SYSTEM

German (ref. 1) describes a disk valve. A remote controlled version of this device has been applied successfully in this research. Due to the plane sealings between the

---

*) standard deviation

disks, the maximum working pressure is 50 kg/cm^2 at 100°C. The sampling volume is constant at fixed temperature and pressure.

During the intermediate stage in the "sandwich" procedure the disk valve is guarded against the high pressure in the reactor by the developed "cryogenic capillary hair pin" valve.

The "cryogenic capillary hair pin" valve

A stainless steel capillary with an internal diameter of .5 mm and an external diameter of 1.6 mm is bent like a hair pin. A co-axial heating wire is wound around the hair pin and a co-axial thermo couple. The temperature of the hair pin can be controlled by a circuit composed of the thermo couple, a controller and the heating wire.

To close the valve, the temperature control system must be switched off and the hair pin has to be immersed in liquid nitrogen. The contents of the capillary tube solidifies and the passage is blocked.

To open the valve, the liquid nitrogen has to be removed and the temperature control system must be switched on to liquidefy the contents. Thus the passage is opened and the contents of the capillary tube is kept at a constant temperature.

The advantages of this method are reliability, absence of dead angles and applicability up to very high pressures.

5.5 PERFORMANCE OF THE KINETIC "SANDWICH" EXPERIMENTS

The "sandwich" experiments have been performed analogous to the low-pressure experiments described by German (ref. 1) with exception of:

- the filling procedure of the reactor with monomers, solvent and initiator,

- the termination of the process,
- the sampling method.

Introduction of the components into the reactor

First the reaction chamber and the compartment for pressure control are heated up to the desired reaction temperature level and evacuated. The pressurizing liquid (*iso*-propylalcohol) is sucked into the pressure control system by the vacuum. From a gascylinder, ethylene gas is admitted into the reaction chamber. At the moment the bellows are pressed together, the pressurizing compartment is shut off to prevent damage by an excessive pressure difference across the bellows. When the pressure is reached that corresponds with the desired amount of ethylene gas (ref. 3), the gas supply stream to the reaction chamber is shut off. Then a mixture of the solvent and the vinylacetate that contains the radical initiator is pumped into the reaction chamber by a diaphragm pump. Pumping is continued until all gaseous monomer is dissolved and the required reaction pressure is almost reached. The required pressure level is reached and maintained by switching the pressure control system into circuit.

Termination of the process

At the end of the experiment, the set-point of the pressure control system is lowered, until the pressure level is reached at which the gaseous monomer has been pressed into the reaction chamber. Then the pressure control is put out of circuit and the contents of the reaction chamber are frothed out by the gaseous monomer.

To rinse the reaction chamber gaseous monomer is admitted and warm solvent is pumped into the reaction chamber. Next the contents are stirred and frothed out.

In order to keep the reaction chamber in good condition, it is filled with solvent containing some initiator when not in use.

Sampling from the reactor

Only during the low-pressure stages, samples are taken from the reaction mixture. During the intermediate stages the sampling valve is isolated from the reactor by the "cryogenic capillary hairpin" valve.

Prior to any injection, the capillary sampling tube was flushed by an amount of reaction mixture slightly larger than the volume of this tube. This had to be done very carefully in order to prevent phase separations in the capillary tube because of its narrow diameter and the viscosity of the reaction mixture.
The maximum displacement of the Teflon bellows permits only a limited volume to be sampled from the reaction chamber.

Because of absorption effects between the copolymer and the volatile components vinylacetate and *iso*-propylalcohol, baseline recovery of these peaks is not complete and the tail of these peaks remains almost parallel to the extrapolated former baseline for a long time. As the integration process is stopped by the integrator at the moment that the peak-slope deceeds a pre-set value, a part of the tailing is not registered by the integrator. Thus systematic deviations are introduced, which will be discussed (cf. Appendix II) and taken into account (cf. 5.9).
By remaining the sample chamber in the carrier gas stream for only 10 seconds, an optimal baseline recovery has been obtained under the given circumstances, and the best conditions have been created for the analysis of the next sample.

5.6 PRESENTATION OF THE EXPERIMENTAL DATA, PRELIMINARY TRANSFORMATIONS AND THE CONCENTRATION REGIONS COVERED BY THE "SANDWICH" EXPERIMENTS

5.6.1 ANALYSIS CONDITIONS

The analysis conditions are identical to those listed by German (ref. 1) and have been kept constant throughout the performance of all kinetic "sandwich" experiments.

5.6.2 PROCESS CONDITIONS

Throughout all kinetic "sandwich" experiments the listed process conditions were kept constant:

- reaction temperature	$62^{\circ}C \pm .2$
- pressure during low pressure stages	$35\ kg/cm^2 \pm .5$
- pressure during intermediate stages	$600\ kg/cm^2 \pm 10$

Specific conditions for each kinetic "sandwich" experiment are the pressure of the ethylene, when admitted into the empty reactor, and the absolute amount of vinylacetate, *tert*-butylalcohol and initiator pumped into the vessel. These conditions are given in Table 5-1.

Experimental code	amount of vinylacetate in cm^3	amount of *tert*-butylalcohol in cm^3	amount of initiator in g	pressure of ethylene in kg/cm^2
A	50	320	1.0	33
B	50	320	.8	20
C	45	280	.7	10
D	27	275	.9	31
E	28	310	1.2	20
F	57	365	1.0	10
G	32	360	.9	30
H	54	350	.6	8

Table 5-1 Specific process conditions.

5.6.3 DATA FROM THE KINETIC "SANDWICH" EXPERIMENTS AND BASIC TRANSFORMATIONS

Each kinetic experiment yields a series of peak areas versus time. In behalf of subsequent calculations, basic transformations have to be carried out. Those referring to experiment A are given as an example in Table 5-2.

time min/10	A_{es} counts	A_{vs} counts	A_{bs} counts	$q = n_e/n_v$	F_v
280	132665	193549	1377179	1.1977	0
468	131740	190714	1384147	1.2070	1.96
593	128924	184022	1391299	1.2241	5.89
737	125510	178134	1394993	1.2311	9.14
898	122389	172362	1382634	1.2407	11.30
1005	120079	167128	1403452	1.2554	15.27
1080	118556	163687	1404186	1.2655	17.06
1170	117093	161106	1405575	1.2700	18.44
1238	115646	158672	1408467	1.2735	19.84
1360	114176	154951	1407230	1.2875	21.65
1443	112455	152155	1414262	1.2914	23.45
time beginning intermediate stage: 1560 min/10 time end intermediate stage: 2358 min/10					
2453	85356	105961	1449175	1.4075	47.97
2526	84615	104234	1452483	1.4184	48.94
2598	83782	102522	1446625	1.4279	49.57
2711	83338	101637	1442497	1.4327	49.87
2852	81409	99071	1440332	1.4358	51.06
3014	80039	96671	1433850	1.4467	52.03
3136	79101	94713	1433016	1.4593	52.97
3237	78478	93296	1427806	1.4698	53.51
3304	77588	91761	1423003	1.4774	54.12
3373	76778	90487	1420292	1.4826	54.67
3440	76360	89159	1413389	1.4965	55.11
3501	75807	88647	1417910	1.4942	55.51
retention time interval vinylacetate peak: 27 min/10 K_{ref} : 1.7473					

Table 5-2 Measurements derived from kinetic "sandwich" experiment A, and basic transformations.

The time basis and the values of A_{es}, A_{vs} and A_{bs} are provided by the digital printer and puncher during each kinetic series. From these values the reaction time is calculated by substracting the retention time from the moment the summet of a sample peak is detected. The monomer feed ratio $q = \frac{n_e}{n_v}$ is calculated by equation (4-7)

$$q = \frac{n_e}{n_v} = \frac{A_{es}}{A_{vs}} * K_{ref} ,$$

the conversion based on vinylacetate is found by combining equations (4-9) and (4-10):

$$F_v = 100 * \left\{ 1 - \frac{A_{vs} * (A_{bs})_o}{A_{bs} * (A_{vs})_o} \right\} \%$$

and finally the points of pressure change have been estimated according to 4.1.2.

In this manner, each low-pressure stage produces a relatively large number (10-20) data $(t_i, q_i, (F_v)_i)$, characterizing the course of the copolymerization reaction. The intermediate stage is characterized by the points of time of pressure change. In order to determine the monomer reactivity ratios, the experimental data will be entered into the computational procedures described in 5.3.

5.6.4 DESCRIPTION OF THE REGION OF MONOMER AND COPOLYMER "CONCENTRATIONS" COVERED BY THE KINETIC "SANDWICH" EXPERIMENTS

In Fig. 5-4 a graphic representation is given of the region of both monomer "concentrations" for all "sandwich" experiments.

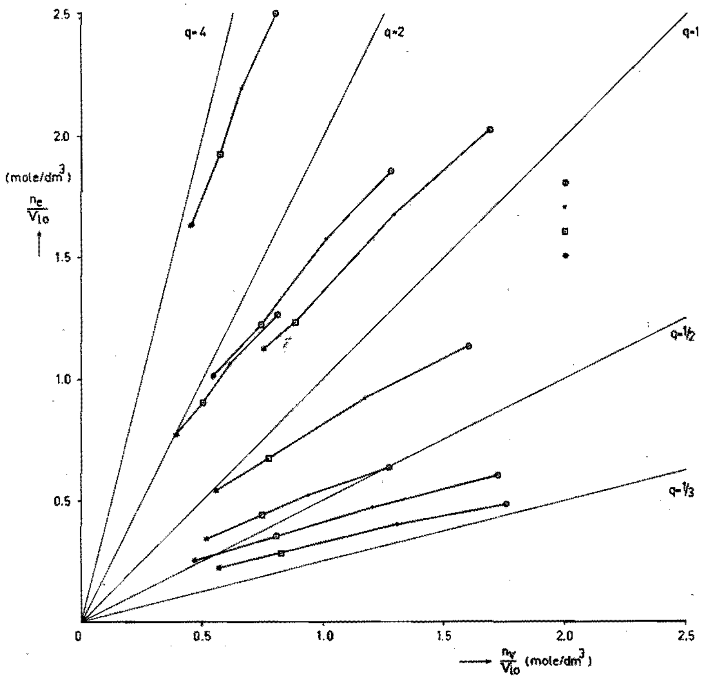

Fig. 5-4 Graphical survey of the monomer "concentration" range covered by the kinetic "sandwich" experiments.

⊙ initial conditions
• beginning intermediate stage
⊡ end intermediate stage
* end conditions

From the figure it can be concluded that:

a for the low-pressure stages:

- the total monomer "concentration" lies between .78 and 3.71 mole/dm^3,
- the monomer feed ratio varies between .27 and 3.49,
- the copolymer "concentration" varies between 0 and 121 g/dm^3,

b for the intermediate stages:

- the total monomer "concentration" lies between 1.10 and 2.96 mole/dm^3,
- the monomer feed ratio varies between .31 and 3.38,
- the copolymer "concentration" varies between 21 and 88 g/dm^3.

5.6.5 PHASE BEHAVIOUR OF THE REACTION MIXTURES

During all kinetic "sandwich" experiments it has been observed that:

- at the start of the experiments the saturating pressure of the reaction mixture was less than the lower reaction pressure level,
- at the end of the experiments the saturating pressure was still less than the lower reaction pressure level,
- samples taken from the vessel during the low-pressure stages showed no turbidity.

Phase behaviour investigations of relevant reaction mixtures at pressures higher than those reported by German (ref. 1) were canceled, because of short of man power resulting from the retrenchment policy. Investigations concerning phase behaviour in the solvent *iso*-propylalcohol, described in Chapter 7, showed no separations up to 3000 kg/cm^2. Although the solidification pressure of *tert*-butylalcohol (1000 kg/cm^2 (ref. 4) at 57°C) is much lower than that of *iso*-propylalcohol it seems reasonable to expect no separations at 62°C and 600 kg/cm^2 in the present study. This presupposition is supported by the fact that no deviations of simple mass law descriptions have been observed.

Concluding it may be stated that:

- during the low-pressure stages no phase separations have taken place;

- it is reasonable to assume that no phase separations have taken place during the intermediate stages, although some more investigation might have been useful.

5.7 EVALUATION OF THE RESULTS

Changing of the pressure level at the beginning and end of the intermediate stages causes temporary deviations from the desired reaction temperature. The temperature-time curve has been determined planimetrically. It appeared that the mean offset of the desired reaction temperature during the complete intermediate stages, has been +.4°C. Since the influence of temperature has been determined in Chapter 6, the influence on the r-values can be estimated.

As $\Delta\hat{r}_e \simeq .003 << \text{st.d. } \hat{r}_e$ (cf. 5.7.2)

and $\Delta\hat{r}_v \simeq .002 << \text{st.d. } \hat{r}_v$ (cf. 5.7.2)

the deviation may be neglected.

5.7.1 EVALUATION OF THE LOW-PRESSURE r-VALUES

The series of kinetic data (q, F_V) resulting from the initial stages have been treated according to F.C.A. methods-A and -B. The final stages have been treated analogously. According to F.C.A. method-B the r-values are:

initial stages	final stages
$\hat{r}_e = .710$	$\hat{r}_e = .750$
$\hat{r}_v = 1.578$	$\hat{r}_v = 1.625$

The residual least-squares sums resulting from F.C.A.

methods-A and -B, which enable application of the model-fitting test (cf. Appendix I), and estimates for $\hat{q}_{sk}$ are listed in Table I-1.
Moreover, these kinetic data have been treated *simultaneously* according to F.C.A. method-B.

initial and final stages *simultaneously*,

$\hat{r}_e$ = .728 st.d. .003
$\hat{r}_v$ = 1.597 st.d. .004

whereas German (ref. 1) reported

$\hat{r}_e$ = .743 st.d. .005
$\hat{r}_v$ = 1.515 st.d. .007

Additional statistical information resulting from this treatment is listed in Table I-2.

From statistic considerations in Appendix I, it appears that small systematic deviations, which are almost equivalent for the three r-value evaluations given so far, are present.

The r-values concerned and their joint confidence regions are plotted in Fig. 5-5.

5.7.2 EVALUATION OF THE HIGH-PRESSURE r-VALUES

The low-pressure r-values have been estimated from the low-pressure stages (cf. 5.7.1). This information, together with the experimental $q - t$ data, have made it possible to determine the beginning and end co-ordinates of the intermediate high-pressure stages of the different kinetic "sandwich" experiments (cf. 5.3.3).

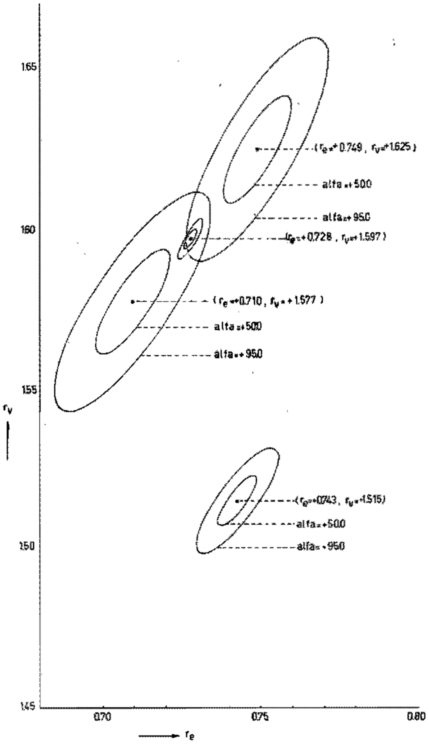

Fig. 5-5 Joint confidence regions resulting from F.C.A. method-B. α = probability level, for example $\alpha = 95\%$, means by definition: If a sufficiently large number of complete experimental series has been carried out and the modelfunction is correct and linear in the parameters, then in one out of twenty cases the (unknown) actual pair of r-values is situated outside the computed confidence region. If the modelfunction is not linear in the parameters, then this result is only valid in first approximation.

initial stages : $\hat{r}_e = .710$, $\hat{r}_v = 1.577$
final stages : $\hat{r}_e = .749$, $\hat{r}_v = 1.625$
joint low-pressure stages: $\hat{r}_e = .728$, $\hat{r}_v = 1.597$
German (ref. 1) : $\hat{r}_e = .743$, $\hat{r}_v = 1.515$

These results have been treated according to F.C.A. method-B.

The following r-values have been found:

intermediate high-pressure stages	relevant low-pressure stages (cf. 5.7.1)
$\hat{r}_e = .91$ st.d. .02	$\hat{r}_e = .728$ st.d. .003
$\hat{r}_v = 1.47$ st.d. .03	$\hat{r}_v = 1.597$ st.d. .004

The residual least-squares sums are listed in Tables I-4 and I-5. These r-values and their joint confidence regions are plotted in Fig. 5-6.

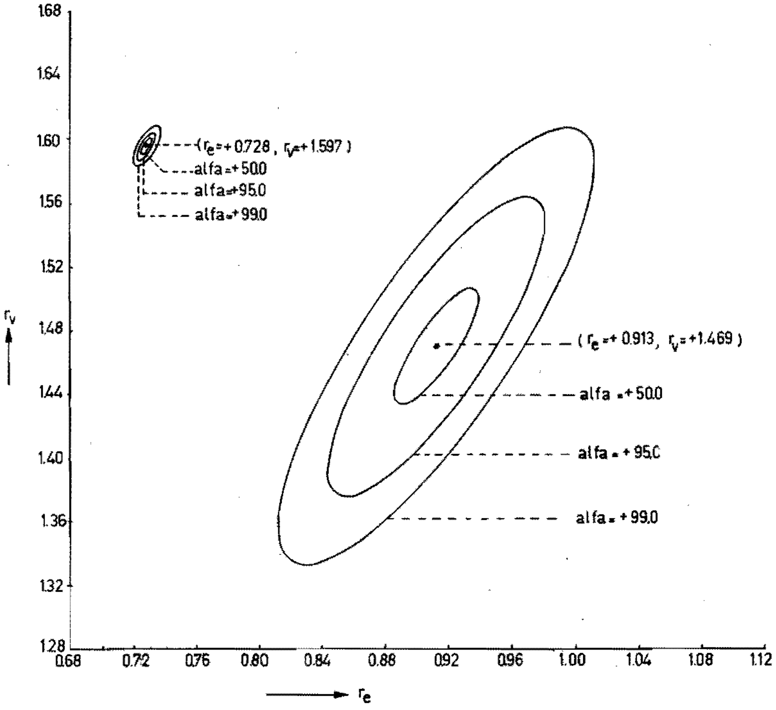

Fig. 5-6 Joint confidence regions resulting from F.C.A. method-B.
α is defined in the legend for Fig. 5-5.
Joint low-pressure stages at 62°C and 34 kg/cm^2:
$\hat{r}_e = .728$, $\hat{r}_v = 1.597$
Intermediate high-pressure stages at 62°C and 600 kg/cm^2:
$\hat{r}_e = .913$, $\hat{r}_v = 1.469$

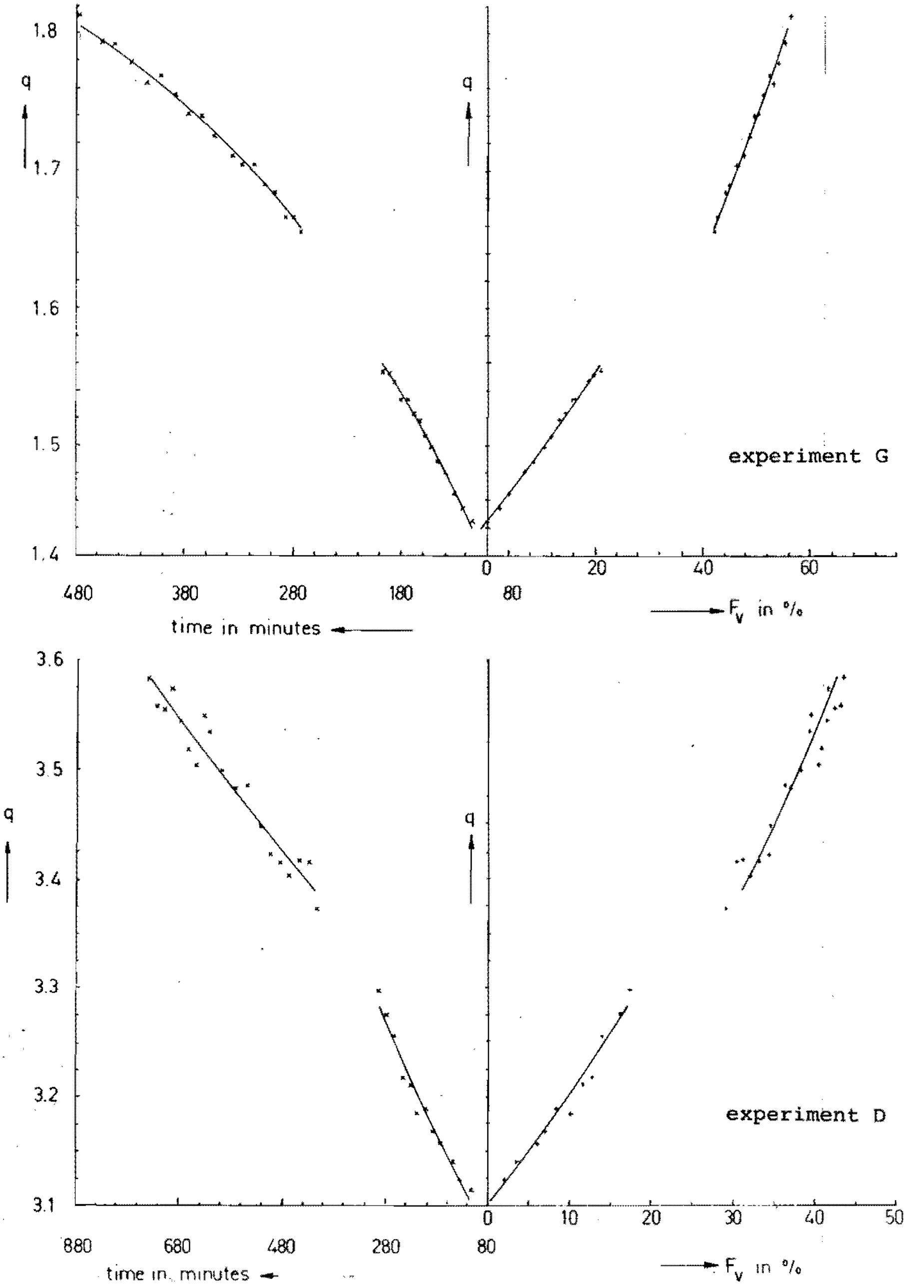

Fig. 5-7 Molar feed ratio q plotted versus degree of conversion F_v (regression curve generated according to F.C.A. method-B) and versus reaction time (regression curve generated according to 5.3.3.1):

In Fig. 5-7 the regression curves through the data points (t, q) and (q, F_v) , gathered during the kinetic "sandwich" experiments G and D, are shown as examples.

5.8 DISCUSSION OF THE RESULTS

From Fig. 5-6 it can be seen that the effect of pressure on the r-values is present. Moreover, the values of $\hat{r}_e$ and $\hat{r}_v$ move in opposite directions under the influence of pressure. So far the expectations of Chapter 2 have been fulfilled.
More careful inspection of the r-values, particularly in comparison with the low-pressure results reported by German, leads to the following considerations.

Application of the model-fitting test (cf. Appendix I) showed significantly that the Alfrey model is not entirely in compliance with the experimental data gathered during the low pressure stages. However, it has been proved by German (ref. 1) at 62°C, and by this research at 75°C (cf. Chapter 6) that the Alfrey model should give an excellent description of the kinetics under these circumstances. It can be concluded that systematic deviations are introduced by the analytical procedure (cf. 5.5).
Now, particularly for vinylacetate, tailing has been found as conversion increases. This indicates absorption of this monomer by the copolymer that has been deposited during evaporation of the sample.
Owing to the principles of the integrating system, parts of these tails are not registered. Consequently, as conversion increases, increasing fractions of vinylacetate will not be measured. These amounts are considered to be proportional to the amount of vinylacetate in the copolymer. At high conversions, in the final stages of every kinetic "sandwich"

run, the concentration of vinylacetate is also thought to be of influence on the losses, and the deviations found are assumed to be proportional to the concentration of vinylacetate monomer and to the amount of vinylacetate in the copolymer.
After introduction of a mathematical correction for these analytical errors in the low-pressure data, corrected low- and high-pressure r-values can be found.
For acceptable values of the adjustment constants in the model function by which the analytical errors have been estimated, low-pressure r-values that are nearly equal to those reported by German are found. This method of evaluation is discussed in Appendix II, the results are discussed in the next section.

5.9 FURTHER PRESENTATION OF THE RESULTS AND DISCUSSION

In the next table and in Fig. 5-8 the results at low and high pressures after corrections as discussed above, are given:

corrected low-pressure stages/		corrected high-pressure stages	
$62^\circ C$	$35\ kg/cm^2$	$62^\circ C$	$600\ kg/cm^2$
$\hat{r}_e$	= .750 st.d. .003	$\hat{r}_e$	= .94 st.d. .04
$\hat{r}_v$	= 1.520 st.d. .004	$\hat{r}_v$	= 1.20 st.d. .04
$\hat{r}_e * \hat{r}_v$	= 1.140 st.d. .008	$\hat{r}_e * \hat{r}_v$	= 1.13 st.d. .09

from which it follows that:

$\Delta V_{ee}^{\#} - \Delta V_{ev}^{\#} = - 11.3\ cm^3/mole$ st.d. 2.1

$\Delta V_{vv}^{\#} - \Delta V_{ve}^{\#} = + 11.9\ cm^3/mole$ st.d. 1.9

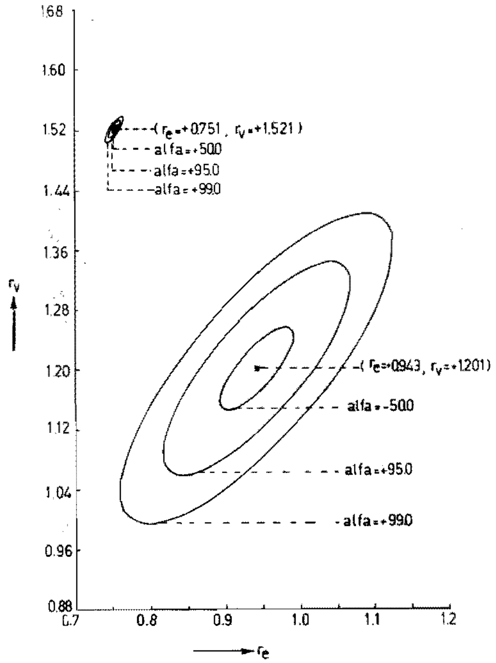

Fig. 5-8 Joint confidence regions resulting from F.C.A. method-B. α is defined in the legend for Fig. 5-5.
Joint corrected low-pressure stages at 62°C and 34 kg/cm^2:

$$\hat{r}_e = .751 \quad , \quad \hat{r}_v = 1.521$$

Corrected intermediate high-pressure stages at 62°C and 600 kg/cm^2:

$$\hat{r}_e = .943 \quad , \quad \hat{r}_v = 1.201$$

with the variance-covariance matrix

for the low pressure stages: for the high pressure stages:

$$\begin{array}{c|cc} & \hat{r}_e & \hat{r}_v \\ \hat{r}_e & .73 * 10^{-5} & .85 * 10^{-5} \\ \hat{r}_v & .85 * 10^{-5} & .16 * 10^{-4} \end{array} \qquad \begin{array}{c|cc} & \hat{r}_e & \hat{r}_v \\ \hat{r}_e & .16 * 10^{-2} & .14 * 10^{-2} \\ \hat{r}_v & .14 * 10^{-2} & .20 * 10^{-2} \end{array}$$

Assuming that the correction procedure for the analytical error is allowed, it can be concluded that $\hat{r}_e * \hat{r}_v$ is independent of pressure.

The differences between the activation volumes of the homo and the cross propagation can be calculated by equation (2-23). These values are equal but opposite in sign for the two kinds of chain radicals. So the activation volumes of the different propagation steps seem to be additions of the individual activation volumes of the monomers and radicals, since the latter obviously do not depend on the kind of transition state involved.

Assuming that the hypothesis of the "monomer activation volume scheme" (cf. 2.2.5) holds, the difference between the individual monomer activation volumes can be calculated:

$$\boxed{\Delta V_{ev}^{*} = \Delta V_{e}^{\#} - \Delta V_{v}^{\#} = -\ 11.6\ \text{cm}^3/\text{mole st.d. } 1.4}$$

Luft (ref. 5) reported the activation volume of the ethylene homo-propagation step up to 2000 kg/cm^2 and found that this value is independent of temperature.

Weale (ref. 6) reported an approximate value of the activation volume of the vinylacetate homo-propagation step at 30°C up to 2000 kg/cm^2.

From these values the activation volumes of the cross-propagation steps have been calculated:

$\Delta V_{ee}^{\#} = -\ 15.6$ cm^3/mole (ref. 5), $\Delta V_{ev}^{\#} = -\ 4$ cm^3/mole,

$\Delta V_{vv}^{\#} = -\ 9$ cm^3/mole (ref. 6), $\Delta V_{ve}^{\#} = -\ 21$ cm^3/mole.

So it can be concluded that:

$r_e = k_{ee}/k_{ev}$ increases with pressure as

$$\frac{d \ln k_{ee}}{dp} > \frac{d \ln k_{ev}}{dp}\text{, whereas:}$$

$r_v = k_{vv}/k_{ve}$ decreases with pressure as

$$\frac{d \ln k_{vv}}{dp} < \frac{d \ln k_{ve}}{dp}\ .$$

As a general result the relations between monomer feed ratio and copolymer composition are presented in Fig. 5-9.

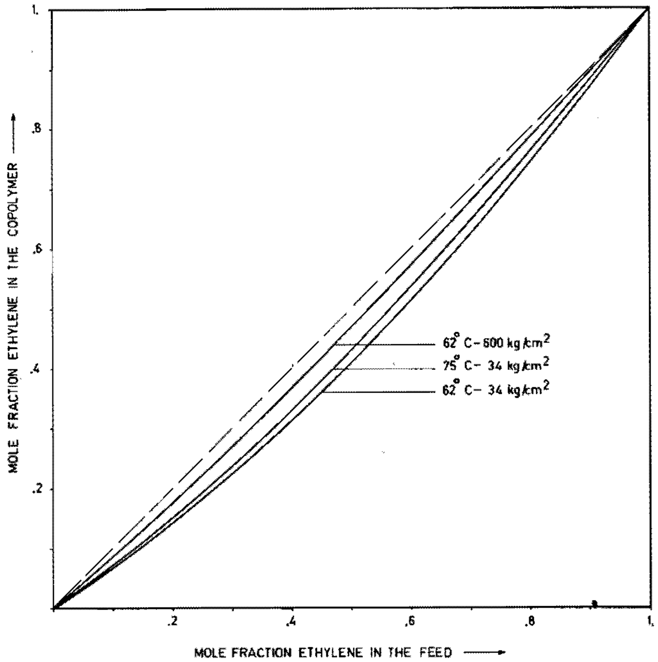

Fig. 5-9 Instantaneous copolymer composition as a function of monomer feed composition.

At 62°C and 34 kg/cm^2 $\hat{r}_e = .743$, $\hat{r}_v = 1.515$
62°C and 600 kg/cm^2 $\hat{r}_e = .94$, $\hat{r}_v = 1.20$
75°C and 34 kg/cm^2 $\hat{r}_e = .833$, $\hat{r}_v = 1.443$
(cf. chapter 6)

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1 A.L. German, *Thesis Eindhoven University of Technology*, (1970) 33.

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3 R.L. Hené, *Internal Report Eindhoven University of Technology*, (1969) 33.

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CHAPTER 6

INFLUENCE OF TEMPERATURE ON THE r-VALUES

6.1 INTRODUCTION

By compression and decompression of the reaction mixture a temperature peak and dip are generated at the beginning and end of the intermediate stage of a "sandwich" experiment (cf. 5.7.2). In behalf of the estimation of the systematic deviations in the r-values, the temperature dependence of the r-values had to be determined. Therefore the experiments carried out by German (ref. 1) at 35 kg/cm^2 and 62°C have been repeated at 35 kg/cm^2 and 75°C. The differences between the activation enthalpies of the homo and cross propagation steps that describe the temperature dependence of the r-values (cf. 2.2) are calculated by combination of the results reported by German and those obtained during this investigation.

6.2 PROCESS AND ANALYSIS CONDITIONS

Throughout the performance of all kinetic series the fixed process and analysis conditions have been kept equal to those listed by German (ref. 1), with the exception of the initial reaction volume which was 500 cm^3 and the temperature of the reactor, sampling tube and sampling valve which has been kept at 75°C.

The total monomer "concentration" $\frac{n_e + n_v}{V_{t_o}}$ covered by all experiments lies between .88 and 4.30 mole/dm^3, while the monomer feed ratio n_e/n_v varies between .47 and 2.98

(which means that the mole fraction ethylene varies between .32 and .75). The final copolymer concentration varies between 7.9 and 58.1 g/dm^3.

6.3 EVALUATION AND DISCUSSION OF THE RESULTS

The mean values of the degree of polymerization have been determined, with the aid of osmometric pressure measurements. Values of several hundreds have been found, in conformity with the condition of high degree of polymerization as stated in Chapter 2.

The peak areas from the kinetic series have been treated according to F.C.A. methods-A and -B (cf. Chapter 3). In Table 6-1 the quality of the curve fitting provided by both methods is given. In Fig. 6-1 the joint confidence regions resulting from F.C.A. method-B together with those

$\hat{r}_e$ = .833 st.d. .006 $\hat{r}_v$ = 1.443 st.d. .008				
Experimental code	number of input data g_k	(residual sum of the squares of the deviations in F_v)$\cdot 10^{-4}$		initial monomer feed ratio q_{gk}
		F.C.A. method-A	F.C.A. method-B	F.C.A. method-B
A	g_1 = 24	8.7	17.7	.472
B	g_2 = 25	10.8	10.7	2.929
C	g_3 = 16	8.2	12.0	.485
D	g_4 = 27	33.3	33.4	.575
E	g_5 = 19	8.5	7.9	2.026
F	g_6 = 24	17.6	9.7	1.900
$\sum_{k=1}^{6} g_k$	135			
$\sum_{k=1}^{6} F_k \cdot 10^{-4}$		87.1	91.4	
degrees of freedom		117	127	
standard deviation in F_v		.9%	.9%	
model-fitting test cf. Appendix I	F^{10}_{117} (95%) = 1.9 model is in compliance with the data		F = .6	

Table 6-1 Quality of the curve fittings, provided by F.C.A. methods-A and -B, in terms of residual least-squares sums and *F*-value. The meaning of *F*-values is given in the legend for Table I-3.

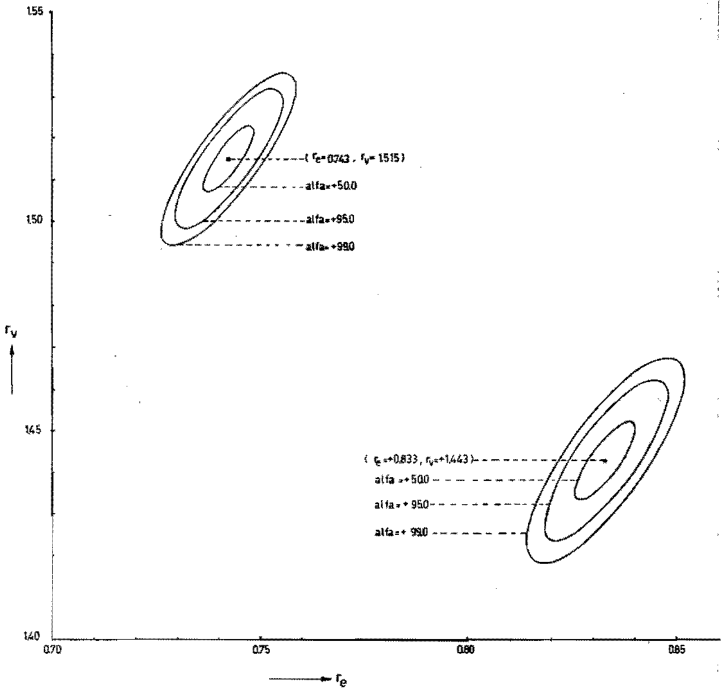

Fig. 6-1 Joint confidence regions resulting from F.C.A. method-B;
62°C and 34 kg/cm^2 (ref. 1): $\hat{r}_e = .743$, $\hat{r}_v = 1.515$;
75°C and 34 kg/cm^2 : $\hat{r}_e = .833$, $\hat{r}_v = 1.443$.

reported by German are shown. The differences between shapes of the joint confidence regions have been caused by the different number of kinetic data (the present research: 135; German: 211), the different number of kinetic runs (the present research: 6; German: 9) and the choice of the initial monomer feed ratios.

It may be concluded that copolymerization of ethylene and vinylacetate at 35 kg/cm^2 and 75°C fits the Alfrey model very well. The quality of the *r*-values determined is comparable with that reported by German at 35 kg/cm^2 and 62°C (cf. Table I-3). Therefore the shift in the *r*-values is caused by the influence of temperature.

The experiments at 35 kg/cm^2 have yielded:

	at $62^{\circ}C$			at $75^{\circ}C$	
$\hat{r}_e =$	.743	st.d. .005	$\hat{r}_e =$	.833	st.d. .006
$\hat{r}_v =$	1.515	st.d. .007	$\hat{r}_v =$	1.443	st.d. .008
$\hat{r}_e * \hat{r}_v =$	1.126	st.d. .013	$\hat{r}_e * \hat{r}_v =$	1.202	st.d. .015

with the estimations of the variance-covariance matrixes

$$\begin{array}{lll} & \hat{r}_e & \hat{r}_v \\ \hat{r}_e & .28 * 10^{-4} & .30 * 10^{-4} \\ \hat{r}_v & .30 * 10^{-4} & .45 * 10^{-4} \end{array} \qquad \begin{array}{lll} & \hat{r}_e & \hat{r}_v \\ \hat{r}_e & .36 * 10^{-4} & .38 * 10^{-4} \\ \hat{r}_v & .38 * 10^{-4} & .63 * 10^{-4} \end{array}$$

So, it follows significantly that $\hat{r}_e * \hat{r}_v$ changes with temperature, while $\hat{r}_e$ and $\hat{r}_v$ change in *opposite* direction (cf. 2.2.4).
Therefore, unlike the activation volumes (cf. 5.9), the activation energies of the different propagation steps cannot be described as an addition of the individual activation energies of the monomers and radicals, since the latter obviously depend on the kind of transition state involved.

For the differences between the enthalpies of activation of the homo and cross propagation steps it has been calculated by a rearranged version of equation (2-25) that

$$\begin{aligned} \Delta H_{ee}^{\#} - \Delta H_{ev}^{\#} &= 2039 \text{ cal/mole st.d. } 180 \\ \Delta H_{vv}^{\#} - \Delta H_{ve}^{\#} &= -\ 869 \text{ cal/mole st.d. } 125 \end{aligned}$$

For the differences between the entropies of activation of the homo and cross propagation steps it has been found by a rearranged version of equation (2-24) that

$$\Delta S_{ee}^{\#} - \Delta S_{ev}^{\#} = 5.49 \text{ cal/mole } ^{o}\text{C st.d. } .55$$

$$\Delta S_{vv}^{\#} - \Delta S_{ve}^{\#} = -1.77 \text{ cal/mole } ^{o}\text{C st.d. } .40$$

REFERENCE

1 A.L. German, *Thesis Eindhoven University of Technology*, (1970).

CHAPTER 7

EXAMINATION OF THE PHASE BEHAVIOUR OF THE SYSTEM ETHYLENE - VINYLACETATE - *ISO*-PROPYLALCOHOL - COPOLYMER

7.1 INTRODUCTION

As already has been pointed out in Chapter 1 and in 5.6.6 the presence of only one (liquid) reaction phase is a condition for the application of the usual models for the description of the kinetics of copolymerization (cf. Chapter 2). For investigations at high pressures, *iso*-propylalcohol was thought to be a better solvent than *tert*-butylalcohol, because the solidification point of *iso*-propylalcohol is much higher than of *tert*-butylalcohol (1000 kg/cm^2 at 62°C (ref. 1)).

Therefore experiments to determine the phase behaviour of the system ethylene - vinylacetate - *iso*-propylalcohol - copolymer have been carried out at the Physics Department of the Delft University of Technology *).
In view of the determination of the kinetics at low pressure in *iso*-propylalcohol (cf. Chapter 8), the vapour pressure of mixtures relevant to the kinetic experiments have been determined accurately for temperatures between 52°C and 70°C. Also four mixtures, with different compositions, have been observed at 62°C and pressures from 500 to 4000 kg/cm^2. At these pressures an accurate determination of the phase behaviour is difficult, because of rapid copolymerization, causing changes in the composition of the sample. Notwithstanding, indications have been found up to which pressure no separations have to be expected.

A description of the apparatus and methods used can be found in literature (ref. 2, 3, 4).

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*) The experiments have been carried out with kind permission of Prof. Dr. Ir. G.A.M. Diepen.

7.2 EVALUATION AND DISCUSSION OF THE RESULTS

To hinder copolymerization of the samples, the samples have been prepared under a nitrogen atmosphere. Nevertheless copolymer has been found after low-pressure duration tests up to two weeks and after high-pressure investigations during some hours up to 4000 kg/cm^2.

In Table 7-1 the initial compositions covered by the experiments have been listed, mentioning the mole ratio n_v/n_i and the mole fraction ethylene $N_e = n_e/(n_e + n_v + n_i)$.

Experimental code		n_v/n_i	$N_e * 10^{-3}$	$N_v * 10^{-3}$
		mole ratio	mole fraction	mole fraction
I	a	0	0	0
	b	0	22.0	0
	c	0	65.2	0
	d	0	106	0
II	a	.026	0	24.9
	b	.026	21	24.4
	c	.026	44.4	23.9
	d	.026	85.2	22.8
III	a	.054	0	51.0
	b	.054	64.3	50.0
	c	.054	112	47.8
	d	.054	145	45.2
IV	a	.184	0	97.7
	b	.184	25.3	95.3
	c	.184	68.7	91.1
	d	.184	111	87.0
V	a	.026	15.6	25.0
	b	.026	97.0	22.8
	c	.055	11.5	52.0
	d	.055	434	29.5

Table 7-1 Survey of the parameters characterizing the samples:
I through IV low-pressure phase behaviour has been determined,
V high-pressure phase behaviour has been observed up to 4000 kg/cm^2.

The low-pressure experiments for the determination of the vapour pressure as a function of composition and temperature have been carried out in a so-called Cailletet tube (ref. 2). From duration tests up to two weeks it appeared that small amounts of copolymer formed do not affect vapour pressure. In the temperature interval 52-70°C, the temperature dependence of the vapour pressure appears to be a straight line within experimental error.

Under condition that $0 \leqslant N_e \leqslant .1$ and $0 \leqslant N_v \leqslant .1$, and at fixed temperature and fixed n_v/n_i ratio, the relation between vapour pressure p_{vapour} and mole fraction ethylene N_e can be described within experimental error by

$$p_{\text{vapour}} = p(N_e = 0) + H * N_e$$

in which $p(N_e = 0)$ = vapour pressure when $N_e = 0$,
H = a Henry constant.

$p(N_e = 0)$ and H depend on temperature and n_v/n_i ratio. In Fig. 7-1 these relations are shown graphically.

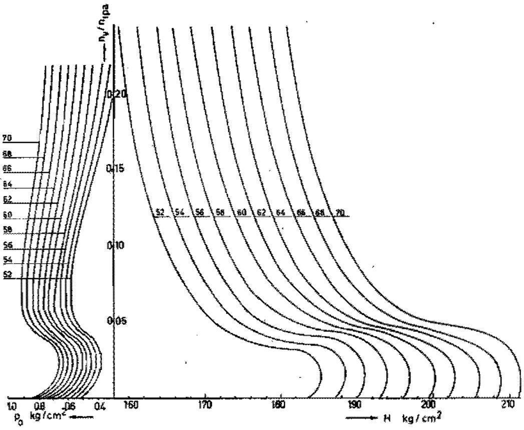

Fig. 7-1 Graphical relations at several temperatures, between n_v/n_{ipa} and $P_o = P(N_e = 0)$, and between n_v/n_i and H.

The exploring experiments up to 4000 kg/cm^2 have been carried out in a special autoclave fitted with "securit" windows (ref. 2).

From visual observations at 62°C it has been found that reversible liquid-liquid phase separations can be expected at pressures over 3000 kg/cm^2. At these pressure levels the copolymerization rate is much higher than at low pressure and copolymerization takes place in both phases. Obviously precipitation of solid phases, only occurs when a second liquid phase is present. Therefore it seems reasonable to expect no separations up to 3000 kg/cm^2 in *iso*-propylalcohol.

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2 F. de Kok, *Internal Report Eindhoven University of Technology*, (1969).
3 L. Aaldijk, *Thesis Delft University of Technology*, (1971) 29.
4 J. Visser, *Internal Report Delft University of Technology*, (1965) 3.

CHAPTER 8

INFLUENCE OF *ISO*-PROPYLALCOHOL ON THE KINETICS

8.1 INTRODUCTION

For future copolymerization experiments with ethylene and vinylacetate, planned to be carried out at pressures over 1000-1500 kg/cm^2, *iso*-propylalcohol was thought to be a better solvent than *tert*-butylalcohol. The phase behaviour in this solvent has been determined (cf. Chapter 7).

Since the chain-transfer coefficient of *iso*-propylalcohol is higher than that of *tert*-butylalcohol (to vinylacetate respectively $.446 * 10^{-2}$ and $.12 * 10^{-3}$ at 70°C (ref. 1)), copolymers with a lower degree of polymerization were expected. To test whether the assumption of sufficiently high degree of polymerization (cf. Chapter 2) holds in this case, the kinetic experiments in *tert*-butylalcohol reported by German (ref. 2) have been repeated in *iso*-propylalcohol.

The results of the vapour pressure measurements given in Chapter 7 have been used to compose the mixtures accurately.

8.2 EVALUATION AND DISCUSSION OF THE RESULTS

The mean values of the degree of polymerization have been determined, with the aid of osmometric pressure measurements. Values of approximately one hundred have been found.

The peak areas have been treated according to F.C.A. methods-A and -B (cf. Chapter 3).

The following r-values have been found at 62°C and 35 kg/cm^2:

tert-butylalcohol (ref. 2)	*iso*-propylalcohol
$\hat{r}_e$ = .743 st.d. .005	$\hat{r}_e$ = .752 st.d. .005
$\hat{r}_v$ = 1.515 st.d. .006	$\hat{r}_v$ = 1.483 st.d. .004

In Table 8-1 the quality of the curve fitting provided by both methods is given. It has been proved significantly by results of the model-fitting test (cf. Table 8-1) that the Alfrey model does not fit these data very well, while those reported by German (ref. 2) are excellently described by this model (cf. Table I-3). The joint confidence regions resulting from F.C.A. method-B and those reported by German are plotted in Fig. 8-1. They do not overlap significantly and thus support the results of the model-fitting test.

$\hat{r}_e$ = .752 st.d. .005	$\hat{r}_v$ = 1.483 st.d. .004			
Experimental code	number of input data g_k	(residual sum of the squares of the deviations in F_v)·10^{-4}		initial monomer feed ratio ϑ_{ak}
		F.C.A. method-A	F.C.A. method-B	F.C.A. method-B
A	g_1 = 20	16.0	21.0	1.496
B	g_2 = 23	17.5	19.9	3.047
C	g_3 = 23	27.7	28.5	1.112
D	g_4 = 22	3.8	6.8	.892
E	g_5 = 21	1.3	1.6	.179
F	g_6 = 23	5.2	5.6	.105
G	g_7 = 20	4.4	6.4	.291
H	g_8 = 21	2.3	14.3	.444
I	g_9 = 19	1.6	15.5	2.060
$\sum_{k=1}^{9} g_k$	192			
$\sum_{k=1}^{9} P_k \cdot 10^{-4}$		79.8	119.6	
degrees of freedom		165	181	
standard deviation in F_v		.7%	.8%	
model-fitting test cf. Appendix I	F_{185}^{16} (95%) = 1.7 F = 5.1 model is not in compliance with the data			

Table 8-1 Quality of the curve fittings, provided by F.C.A. methods-A and -B, in terms of residual least-squares sums and F-value. The meaning of F-values is given in the legend for Table I-3.

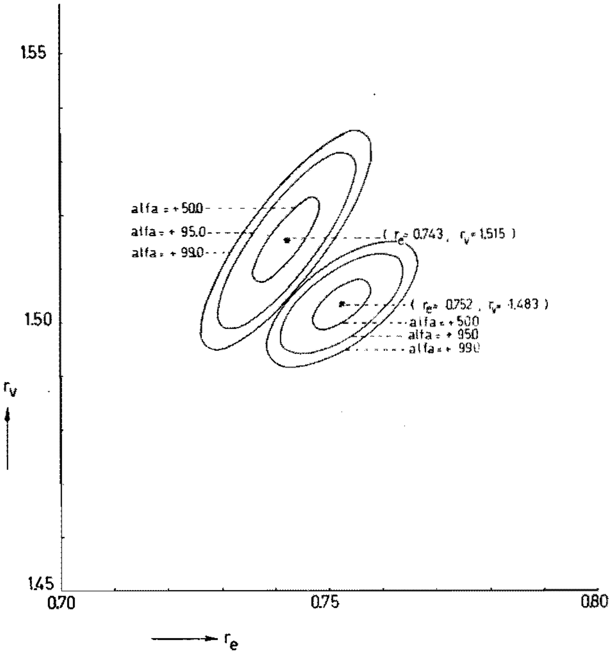

Fig. 8-1 Joint confidence regions resulting from F.C.A. method-B;
tert-butylalcohol (ref. 2): $\hat{r}_e = .743$, $\hat{r}_v = 1.515$;
iso-propylalcohol : $\hat{r}_e = .752$, $\hat{r}_v = 1.483$.

It has been observed that:

- Under identical reaction conditions 5 to 8 times higher degrees of polymerization have been reported in *tert*-butylalcohol by German (ref. 2).
- *Iso*-propylalcohol is not a retarder (copolymerization rate did not deviate significantly from the rate in *tert*-butylalcohol).

Therefore, it may be concluded that termination and initiation steps have been dominated by termination due to transfer to the solvent and reinitiation by the solvent radicals.

The shift in the r-values *might* be explained by the hypothesis that:

- because of the low degrees of polymerization, reinitiation and termination by transfer have violated the Alfrey model noticeably,
- due to transfer to the solvent, relatively more ethylene has been built into the end position of the chain than into the chain itself,
- due to efficient reinitiation by the solvent radicals, more ethylene has been built into the initial position of the chain than into the chain itself.

To test equation (2-1),

$$\frac{dn_e}{dn_v} = \frac{r_e * \frac{n_e}{n_v} + 1}{r_v * \frac{n_v}{n_e} + 1} ,$$

the relative monomer consumption by propagation only should be substituted for dn_e/dn_v .

The analytically determined value also contains the consumptions by initiation, termination and transfer. The last contribution is said to be much larger in *iso*-propylalcohol than in *tert*-butylalcohol.

This leads to

$$\left(\frac{dn_e}{dn_v}\right)_{\text{determined}} > \left(\frac{dn_e}{dn_v}\right)_{\text{pure propagation}}$$

and thus that

$$(r_e)_{\text{determined}} > (r_e)_{\text{pure propagation}}$$

$$\text{and} \quad (r_v)_{\text{determined}} < (r_v)_{\text{pure propagation}} .$$

REFERENCES

1 G.E. Ham, *Vinyl Polymerization*, 1 (1967) 241, Marcel Dekker, Inc., New York.

2 A.L. German, *Thesis Eindhoven University of Technology*, (1970) 80.

APPENDIX I

ADDITIONAL STATISTICAL INFORMATION RESULTING FROM THE EVALUATION OF THE "SANDWICH" EXPERIMENTS

I.1 A model-fitting test

It is assumed that an experiment has been performed for the purpose of estimating the values of the unknown parameters in a modelfunction, of which the correctness is not in question. On assumption that:

- the independent variable can be determined without error,
- the errors in the dependent variable are independent and normally distributed with mean value zero and variance σ^2 ,

least-squares estimation of the parameters results in a residual sum of squares which is $\sigma^2 \chi^2_{g-p}$-distributed, in which g is the number of observations and p is the number of parameters, estimated from the data.

Definition: χ^2_ν -distributed denotes the chi-square distribution at ν degrees of freedom, it equals the distribution of ν squared independent standard-normal variates.

In case of a modelfunction which is non-linear in the parameters, this result is only valid in first approximation. Symbols used in the derivation are:

n = number of experiments that have been performed,

P_k = residual sum of squares that results from the k-th experiment.

g_k = number of observations in the k-th experiment,

and p = number of parameters in the modelfunction.

Then P_k is $\sigma^2\ \chi^2_{g_k-p}$-distributed, shortly denoted by

$$P_k \sim \sigma^2\ \chi^2_{g_k-p}$$

Thus by definition

$$\sum_{k=1}^{n} P_k \sim \sigma^2\ \chi^2_{\sum\limits_{k=1}^{n}(g_k-p)} = \sigma^2\ \chi^2_{G-n*p}$$

in which G is the total number of observations.

Now it is assumed that r out of the p parameters are equal for all n experiments. Thus the n experiments are considered as *one* experiment with $n*(p-r) + r$ unknown parameters.

Under this assumption the residual sum of the squares P is

$$\sigma^2\ \chi^2_{G-(p-r)*n-r} \text{ - distributed.}$$

P can be decomposed:

$$P = \sum_{k=1}^{n} P_k + (P - \sum_{k=1}^{n} P_k)$$

The left hand side is $\sigma^2\ \chi^2_{G-(p-r)*n-r}$-distributed and the first term in the right hand side is $\sigma^2\ \chi^2_{G-n*p}$-distributed. Moreover it is obvious that:

$$P - \sum_{k=1}^{n} P_k > 0 \ .$$

Then it follows, according to a well-known theorem (ref. 1):

$$P - \sum_{k=1}^{n} P_k \sim \sigma^2 \ \chi^2_{G-(p-r)*n-r-(G-n*p)} = \sigma^2 \ \chi^2_{r*(n-1)}$$

and independent of $\sum_{k=1}^{n} P_k$.

If $c \sim \chi^2_{\nu_1}$ and $d \sim \chi^2_{\nu_2}$ and independent,
then

$$\frac{c/\nu_1}{d/\nu_2} \sim F^{\nu_1}_{\nu_2}$$

in which $F^{\nu_1}_{\nu_2}$ denotes the F-distribution on ν_1 and ν_2 degrees of freedom (tabulated in ref. 2).
According to this the unknown σ^2 has been eliminated, thus yielding:

$$F = \frac{(P - \sum_{k=1}^{n} P_k)/(r*(n-1))}{\sum_{k=1}^{n} P_k/(G-n*p)} \sim F^{r*(n-1)}_{G-n*p}(\alpha) = F^{b-a}_{a}(\alpha)$$

A large value of this statistic (depending on the chosen significance level α) leads to rejection of the assumption that all r parameters are common to all n experiments.

I.2 The model-fitting test applied to the low-pressure stages of the "sandwich" experiments (cf. Chapter 5)

The kinetic data (q, F_v) gathered during:

- the initial stages of the "sandwich" experiments,
- the final stages of the "sandwich" experiments,
- low-pressure experiments, reported by German (ref. 3),

have been treated according to F.C.A. methods-A and -B. The residual least-squares sums and the initial monomer feed ratios resulting from the initial and final stages are listed in Tables I-1 and I-2.

	initial stages r_e = .710 st.d. .010 r_v = 1.577 st.d. .014				final stages r_e = .749 st.d. .009 r_v = 1.625 st.d. .014			
Experimental code	g_k	F.C.A.-A	F.C.A.-B		g_k	F.C.A.-A	F.C.A.-B	
		P_k*10^{-4}	P_k*10^{-4}	$\hat{q}_{sk}$		P_k*10^{-4}	P_k*10^{-4}	$\hat{q}_{sk}$
A	g_1= 11	2.8	18.7	1.191	g_1= 12	4.2	15.2	1.414
B	g_2= 15	7.5	7.8	.707	g_2= 21	17.6	19.0	.871
C	g_3= 17	12.2	13.1	.501	g_3= 16	13.2	18.0	.594
D	g_4= 12	9.9	10.5	3.097	g_4= 19	45.9	50.3	3.363
E	g_5= 16	18.2	23.4	1.572	g_5= 16	14.3	17.6	1.810
F	g_6= 10	6.6	13.6	.349	g_6= 19	29.2	29.1	.440
G	g_7= 14	2.9	2.8	1.444	g_7= 18	8.5	9.2	1.660
H	g_8= 11	3.4	5.3	.273	g_8= 13	13.3	13.3	.346
$\sum_{k=1}^{9} g_k$	106				134			
$\sum_{k=1}^{9} P_k*10^{-4}$		63.5	95.2			146.2	171.7	
degrees of freedom		82	96			110	124	
standard deviation in F_v		.9%	1.0%			1.1%	1.2%	

Table I-1 Results of the computations, according to F.C.A. methods-A and -B, on the initial stages and on the final stages of the "sandwich" experiments (cf. 5.7.1).

$\hat{F}_e$ = .728 st.d. .003 $\hat{F}_v$ = 1.597 st.d. .004	Experimental code	g_k	model $q(F_v)$	
			$P_k \cdot 10^{-4}$	$\hat{q}_{ek}$
	A_{in}	11	16.9	1.192
	A_{in}	15	7.9	.707
	C_{in}	17	12.9	.500
	D_{in}	12	10.0	3.100
	E_{in}	16	26.1	1.573
	F_{in}	10	14.9	.348
	G_{in}	14	3.1	1.445
	H_{in}	11	4.6	.273
	A_{fin}	12	12.4	1.141
	B_{fin}	21	19.2	.680
	C_{fin}	16	17.7	.492
	D_{fin}	19	50.8	3.023
	E_{fin}	16	15.4	1.551
	F_{fin}	19	29.8	.336
	G_{fin}	18	9.8	1.390
	H_{fin}	13	14.2	.264
$\sum_{k=1}^{8} g_{k\ in} + \sum_{k=1}^{8} g_{k\ fin}$		240		
$\left(\sum_{k=1}^{8} P_{k\ in} + \sum_{k=1}^{8} P_{k\ fin}\right) \cdot 10^{-4}$			265.7	
degrees of freedom			222	
standard deviation in F_v			1.12	
in: initial stages fin: final stages				

Table I-2 Results of the computations, according to F.C.A. method-B, on the joint low-pressure stages of the "sandwich" experiments (cf. 5.7.1).

The model-fitting test has been applied to the residual least-squares sums. The results are listed in Table I-3. It can be seen from this table that the data gathered

- during the initial stages are not in compliance with the modelfunction,
- during the final stages are in compliance with the modelfunction, although *F* is close to the limit value,
- during similar low-pressure experiments, reported by German (ref. 3), fit the modelfunction extremely well.

Since the correctness of the modelfunction has been proved

*ref. 2 subject	degrees of freedom a	b	F	F_a^{b-a} (95%)*
initial stages	82	96	2.9	1.8
final stages	110	124	1.3	1.8
German ref. 3	194	210	.3	1.6

Table I-3 Results of the model-fitting test applied to the residual least-squares sums, resulting from computations according to F.C.A. methods-A and -B (cf. 5.8).

$F_a^{b-a}(\alpha)$, with for example α (probability level) = 95%, means by definition: if a sufficiently large number of complete experimental series has been carried out and the modelfunction is correct and linear in the parameters, then in one out of twenty cases a F-value will be found that exceeds the $F_a^{b-a}(\alpha)$ limit. If the modelfunction is not linear in the parameters, then this result is only valid in first approximation. So, if $F < F_a^{b-a}(\alpha)$ it may be assumed that the modelfunction is in compliance with the data.

model $q(t)$	Experimental code	g_k	P_k*10^{-4}	$\hat{q}_{ek}$	$\hat{S}_k$
	A_{in}	11	1.14	1.193	10.1
	B_{in}	15	.81	.705	3.8
	C_{in}	17	.41	.500	1.7
	D_{in}	12	10.16	3.103	11.5
	E_{in}	16	7.73	1.559	30.7
	F_{in}	10	.19	.351	1.6
	G_{in}	14	1.04	1.440	30.2
	H_{in}	11	.04	.272	1.2
	A_{fin}	12	3.20	1.129	17.1
	B_{fin}	21	7.02	.757	3.2
	C_{fin}	16	1.25	.529	1.3
	D_{fin}	19	48.91	3.234	4.7
	E_{fin}	16	4.67	.854	68.9
	F_{fin}	19	2.31	.386	1.3
	G_{fin}	18	3.22	1.395	40.1
	H_{fin}	13	.44	.297	1.0
$\sum_{k=1}^{8} (g_{k\,in} + g_{k\,fin})$		240			
$\sum_{k=1}^{8} (P_{k\,in} + P_{k\,fin}) * 10^{-4}$			92.54		
degrees of freedom = 208					
(standard deviation in q) $*10^{-3}$ = 6.7					
in: initial stage fin: final stage					

Table I-4

$\hat{P}_e$ = .91 st.d. .02

$\hat{P}_v$ = 1.47 st.d. .03

Experimental code	g_k	P_k*10^{-6}
A	1	8.6
B	1	18.1
C	1	120.0
D	1	24.4
E	1	777.0
F	1	37.5
G	1	411.0
H	1	9.7
$\sum_{k=1}^{8} g_k$	8	
$\sum_{k=1}^{8} P_k*10^{-6}$		1406.3

Table I-5

Table I-4 Results of the computations on the low-pressure q-t data according to 5.3.3.1 (cf. 5.7.2).

Table I-5 Results of the computations on the begin and end co-ordinates of the intermediate high-pressure stages (cf. 5.3.3.2), according to F.C.A. method-B (cf. 5.7.2).

significantly, it may be concluded that the data gathered during the low-pressure stages have been affected by systematic deviations.

To test whether the initial and final stages may be described with the same pair of r-values, the model-fitting test has been applied to the residual least-squares sums resulting from *simultaneous* and *separate* treatment according to F.C.A. method-B. It appeared significantly that *one* pair of r-values may be used.

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2 Duncan, *Quality Control and Industrial Statistics*, (1959) 878, Richard D. Irwin, Inc., Homewood.

3 A.L. German, *Thesis Eindhoven University of Technology*, (1970) 84.

APPENDIX II

CORRECTION OF THE ANALYTICAL ERRORS IN THE LOW-PRESSURE DATA OF THE "SANDWICH" EXPERIMENTS

The experiments described in Chapter 5 and in Appendix III have yielded systematically deviating analytical data. The deviations are assumed to be caused by interaction between copolymer that stays behind in the evaporation chamber of the sampling valve, and components which evaporate from the sample, into the gas chromatograph (cf. 5.8).
Only the affection of the vinylacetate peaks by the copolymer has to be taken into account.
For absolute conversions up to 20% the affection is approximated by the modelfunction

$$n_{vd} = n_{vk} - k_{in} * (n_{vo} - n_{vk}) \qquad \text{(II-1)}$$

in which n_{vo} = initial number of moles v in the reactor,
n_{vk} = number of moles v in the reactor,
n_{vd} = determined number of moles v in the reactor,
k_{in} = dimensionless constant,
$n_{vo} - n_{vk}$ = number of moles v that has been copolymerized = $(n_{vo} * F_v)/100$.

The numbers of moles can be calculated according to equation (4-6).

Starting from the r-values reported by German (ref. 1), the propagation of this deviation model into the r-values has been simulated for several values of k_{in}. The results are shown in Fig. II-1. It appears, that the shift of the r-values corresponds with the shift that has been observed during the initial stages of the "sandwich" experiments (cf. 5.7.1) and the experiments with the electro-magnetic needle valve (cf. Appendix III).

For absolute conversions between 40% and 60%, it appears that modelfunction II-1 yields too strong an affection. Therefore k_{in} has been replaced by $k_f * n_{vk}$, yielding

$$n_{vd} = n_{vk} - k_f * n_{vk} * (n_{vo} - n_{vk}) \qquad \text{(II-2)}$$

in which k_f is not a dimensionless constant

The propagation of this deviation model into the r-values has been simulated for several values of k_f. The results are shown in Fig. II-2. The shift corresponds with the observed shift of the r-values during the final stages of the "sandwich" experiments (cf. 5.7.1).

Fig. II-1

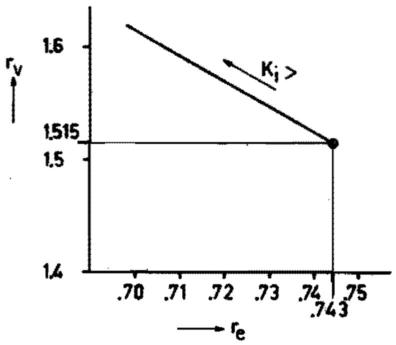

Fig. II-2

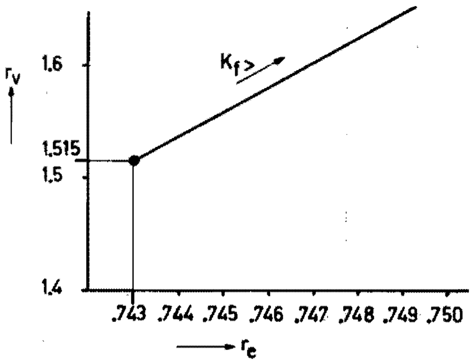

Fig. II-1 Affection of the r-values by model II-1 as a function of the adjustment constant k_i .

Fig. II-2 Affection of the r-values by model II-2 as a function of the adjustment constant k_f .

The correction of the data gathered during the kinetic "sandwich" experiments

The initial stages of the "sandwich" experiments have been corrected according to model I-1 with $k_{in} = .034$.
The corrected r-values are in the same region as those reported by German (ref. 1).
The final stages of the "sandwich" experiments have been corrected according to model II-2 with $k_f = .975$.
The corrected r-values are in the same region as those reported by German (ref. 1) and the corrected r-values which describe the initial stages.
These values of k_{in} and k_f are acceptable because
$k_{in} \simeq k_f * n_{vk}$.

Moreover, these corrected kinetic data have been treated *simultaneously* according to F.C.A. method-B.
The results of this evaluation can be found in Table II-1, section 5.9 and Fig. 5-8.
Analogous to 5.7.2 the high-pressure r-values have been estimated. The results are given in Tables II-2 and II-3, section 5.9 and Fig. 5-8.

The correctness of the modelfunctions

Two different modelfunctions have been used to *approximate* the systematic deviations in the data gathered during the initial and the final stages.
As these deviations can be traced back to the same source, these models can only be *approximations*. Thus it is unlikely that the correctness of the modelfunctions will be confirmed by decreasing residual least-squares sums. So, it is understandable why these sums have been increased from:

$2.7 * 10^{-2}$ (cf. Table I-2) to $3.4 * 10^{-2}$
(cf. Table II-1) for the low-pressure stages,
$1.4 * 10^{-3}$ (cf. Table I-4) to $1.8 * 10^{-2}$
(cf. Table II-3) for the high-pressure stages.

Table II-1

$\hat{r}_e$ = .750 st.d. .003 $\hat{r}_v$ = 1.520 st.d. .004			
Experimental code	g_k	model $q(F_v)$	
		P_k*10^{-4}	$\hat{q}_{sk}$
A_{in}	11	18.2	1.192
B_{in}	15	10.1	.708
C_{in}	17	16.1	501
D_{in}	12	11.8	3.100
E_{in}	16	32.8	1.574
F_{in}	10	15.4	.349
G_{in}	14	4.0	1.446
H_{in}	11	6.7	.273
A_{fin}	12	18.5	1.109
B_{fin}	21	22.5	.662
C_{fin}	16	26.2	.485
D_{fin}	19	70.0	3.009
E_{fin}	16	18.9	1.545
F_{fin}	19	38.8	.326
G_{fin}	18	19.1	1.367
H_{fin}	13	17.8	.256
$\sum_{k=1}^{8} (g_{k\ in} + g_{k\ fin})$	240		
$\sum_{k=1}^{8} (P_{k\ in} + P_{k\ fin})*10^{-4}$		338.9	
degrees of freedom = 222			
standard deviation in F_v = 1.2%			
in: initial stage fin: final stage			

Table II-2

Experimental code	g_k	model $q(t)$		
		P_k*10^{-4}	$\hat{q}_{sk}$	$\hat{\delta}_k$
A_{in}	11	.91	1.194	10.4
B_{in}	15	.78	.706	3.7
C_{in}	17	.41	.500	1.6
D_{in}	12	10.63	3.102	7.9
E_{in}	16	7.45	1.559	39.0
F_{in}	10	.18	.351	1.5
G_{in}	14	.96	1.441	35.1
H_{in}	11	.04	.272	1.1
A_{fin}	12	2.37	1.131	12.8
B_{fin}	21	5.04	.732	2.5
C_{fin}	16	1.03	.519	1.1
D_{fin}	19	45.58	3.190	3.5
E_{fin}	16	4.34	.822	82.9
F_{fin}	19	1.74	.368	1.0
G_{fin}	18	2.60	1.414	33.1
H_{fin}	13	.34	.284	.8
$\sum_{k=1}^{8} (g_{k\ in} + g_{k\ fin})$	240			
$\sum_{k=1}^{8} (P_{k\ in} + P_{k\ fin})*10^{-4}$		84.4		
degrees of freedom = 208				
(standard deviation in q)$*10^{-3}$ = 6.3				
in: initial stages fin: final stages				

Table II-1 Results of the computations, according to F.C.A. method-B, on the corrected joint low-pressure stages (cf. 5.9).

Table II-2 Results of the computations, according to 5.3.3.1, on the corrected q-t data (cf. 5.9).

$\hat{r}_e$ = .94 st.d. .04 $\hat{r}_v$ = 1.20 st.d. .04		
Experimental code	g_k	P_k*10^{-5}
A	1	641
B	1	5
C	1	121
D	1	5
E	1	677
F	1	11
G	1	328
H	1	12
$\sum_{k=1}^{8} g_k$	8	
$\sum_{k=1}^{8} P_k*10^{-5}$		1800

Table II-3

Results of the computations on the corrected begin and end co-ordinates of the intermediate high-pressure stages (cf. 5.3.3.2), according to F.C.A. method-B (cf. 5.9).

REFERENCE

1 A.L. German, *Thesis Eindhoven University of Technology*, (1970).

APPENDIX III

A HIGH-PRESSURE ELECTRO-MAGNETIC SAMPLING VALVE

The author of this thesis developed, tested and applied an electro-magnetic sampling valve that is based on a metallic line sealing. The valve has been designed for application at pressures up to 1000 kg/cm^2. When using line sealing sampling systems can be designed which are applicable up to higher pressures than 1000 kg/cm^2.

III.1 The electro-magnetic needle valve

The principles of the valve are shown in Fig. III-1, taken from ref. 7. The body (17) contains a carrier gas canal. This gas enters the valve at A, flows through the needle shaft into the evaporation chamber B and leaves the valve at C.

The reaction chamber and the sampling valve are connected by the co-axial capillary tubes D and E. The inner tube D is the sampling tube. The outer thick-walled tube E balances pressure differences across thin-walled tube D and its hard-soldered fixing into seat (19).

The sample outlet is shut off by the metallic line sealing formed by the contact between needle (38) and seat (19). The force applied to the needle by springbox (5) can be adjusted by set-knob (1).

The sample outlet can be opened by a blocky rush of current through electro magnet (36) (ref. 1, 2, 4, 6). Needle lift is limited by the clearance between magnet core (45) and the pole piece (34). This clearance can be adjusted by revolving the electro-magnet body (46) in its screw thread

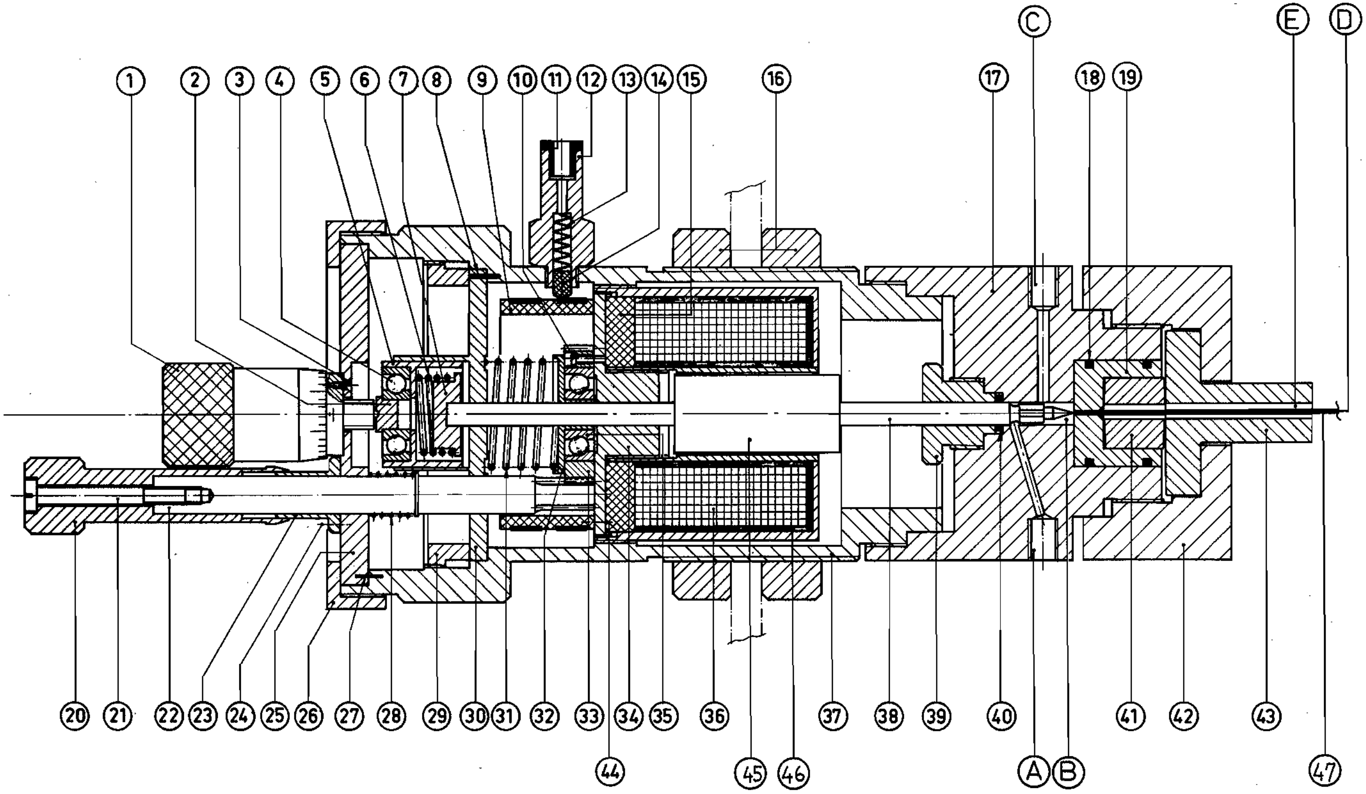

Fig. III-1 Constructional drawing of the high-pressure electromagnetic sampling valve.

fixing into the upper valve body (37). This rotation is controlled by gearing (33) and set-knob (20). The current through the revolvable electro magnet is conducted by the sliding contact construction (9), (14).

Parameters that govern the sample volume

Sample volume is governed by (ref. 1, 2)

- needle lift time,
- needle lift,
- needle top angle,
- sample outlet diameter,
- springbox tension,
- sample density and viscosity,
- reaction pressure.

III.2 Testing of the valve

Using N_2 gas, the valve has been tested during several thousands of injections at pressures up to 300 kg/cm^2 (ref. 2). Already with a fraction of the springbox tension necessary for fast closing (ref. 1), gas chromatographic leak-free operation has been reached. The valve is expected to operate leak-free up to the working pressure (1000 kg/cm^2).

Mixtures of ethylene, vinylacetate and *tert*-butylalcohol have been injected into the gas chromatograph described by German (ref. 5). Repeatability of the peak areas was approximately .1% .

III.3 Application of the valve

In order to test the valve, the copolymerization experiments described by German (ref. 5) have been repeated, using this valve instead of the disk valve (ref. 3, 6). The experimental data have been evaluated according to F.C.A. methods-A and -B. The model-fitting test (cf. Appendix I), applied to the residual least-squares sums, showed that systematic analytical errors are present. The resulting r-values are compared with the correct r-values (ref. 5) in Fig. III-2. It is found that systematic deviations are caused by absorption of vinylacetate at copolymer deposited in the evaporation chamber (cf. section 5.8, Appendix I).

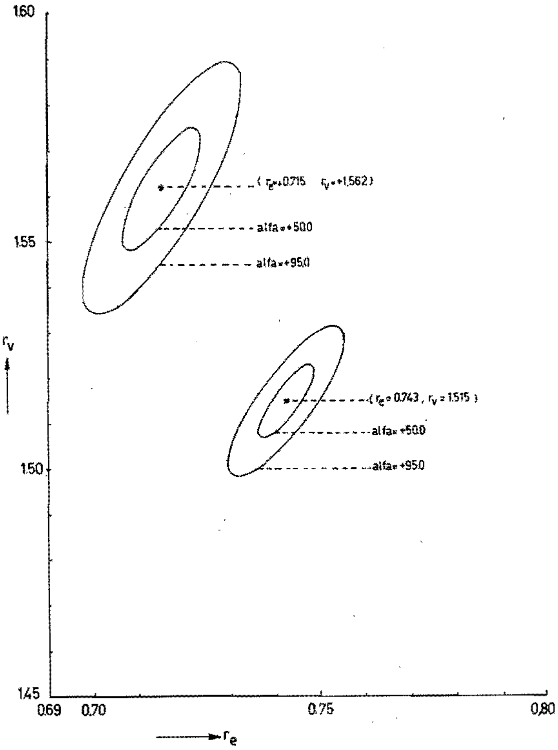

Fig. III-2 Joint confidence regions resulting from F.C.A. method-B; reported correct r-values (ref. 5)

$\hat{r}_e = .743$, $\hat{r}_v = 1.515$

r-values determined with the aid of the sampling valve described here

$\hat{r}_e = .715$, $\hat{r}_v = 1.562$

It is expected that modification of the volume and the shape of the evaporation chamber will lead to considerable reduction of this systematic deviation.

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2 C.F. Braakman, *Internal Report Eindhoven University of Technology*, (1970).

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4 Schematic diagrams Ewpl 204, 205 and 206 Central Technical Service (C.T.D.) *Eindhoven University of Technology*, (1971).

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SUMMARY

This thesis describes an investigation on the pressure dependence of the copolymerization of ethylene and vinylacetate in *tert*-butylalcohol. In behalf of the present and future research the influence of temperature and the type of solvent on the kinetics, as well as the influence of pressure on the phase behaviour have been studied.

The experimental methods are based on sequential quantitative gas chromatographic determination of the feed composition.

In order to determine the pressure dependence of the monomer reactivity ratios (*r*-values) the "sandwich" method has been developed. All experimental runs consist of three stages. In the first stage pressure is kept low (35 kg/cm^2, first stage). At the end of this stage pressure is rapidly raised to the desired high-pressure value (600 kg/cm^2, second stage). At the end of this high-pressure stage pressure is rapidly lowered and the reaction is allowed to succeed in the last stage at low pressure (35 kg/cm^2, third stage). The feed composition during the first and the last stages is followed by sequential sampling. From these data the feed composition at the beginning and the end of the high-pressure stage can be calculated accurately by using non-linear least-squares methods applied to integrated copolymerization equations. So, any run produces two data pairs for the high-pressure stage and two series of data for the low-pressure stages. The combined data of all runs make possible the determination of the *r*-values at high and at low pressure by non-linear least-squares methods. Application of a statistical model-fitting test showed that small systematic analytical errors are present. After cor-

rection of these errors the following r-values have been found

	62°C	35 kg/cm^2			62°C	600 kg/cm^2	
$\hat{r}_e$ =	.750	st.d.	.003	$\hat{r}_e$ =	.94	st.d.	.04
$\hat{r}_v$ =	1.520	st.d.	.004	$\hat{r}_v$ =	1.20	st.d.	.04

The pressure influence leaves $\hat{r}_e * \hat{r}_v$ constant within experimental error. This is in accordance with the hypothesis that reacting monomers and radicals have fixed contributions to the activation volume. These contributions are independent of the transition state in which the reactants participate.

In that case the difference in the contributions of the monomers is

$$\Delta V_e^{\#} - \Delta V_v^{\#} = -\ 11.6\ \text{cm}^3/\text{mole} \quad \text{st.d.} \quad 1.4$$

The above mentioned hypothesis may become the base of a "monomer activation volume scheme". This scheme predicts the pressure influence on the copolymerization of two monomers if the pressure dependence on the copolymerization of each monomer with a third monomer is known experimentally.

This may be also a worthwhile hypothesis for non-polymer reactions.

The investigation of the temperature dependence of the r-values resulted in data which are in compliance with the Alfrey model. The differences in the activation enthalpies and entropies for the propagation steps are

$$\Delta H_{ee}^{\#} - \Delta H_{ev}^{\#} = 2039 \quad \text{cal/mole} \quad \text{st.d.} \quad 180$$

$$\Delta H_{vv}^{\#} - \Delta H_{ve}^{\#} = -\ 869 \quad \text{cal/mole} \quad \text{st.d.} \quad 125$$

$$\Delta S_{ee}^{\#} - \Delta S_{ev}^{\#} = 5.49 \quad \text{cal/mole}\ ^{\circ}\text{C} \quad \text{st.d.} \quad .55$$

$$\Delta S_{vv}^{\#} - \Delta S_{ve}^{\#} = -\ 1.77 \quad \text{cal/mole}\ ^{\circ}\text{C} \quad \text{st.d.} \quad .40$$

The subscript ev for example, refers to the propagation step of the ethylene radical with the vinylacetate monomer.

Because of increased solvent chain transfer the use of *iso*-propylalcohol instead of *tert*-butylalcohol led to lower molecular weights of the copolymer products. Therefore the experimental kinetic data were not completely in accordance with the Alfrey model. The deviation in the r-values estimated from these data has been explained.

Separately, a new sampling valve (electro-magnetic needle valve) has been described, suited for direct sampling from high-pressure systems (1000 kg/cm^2). However, this valve is still in the developmental stage. The present results show somewhat larger systematic deviations than those from the "sandwich" method.

SAMENVATTING

Dit proefschrift beschrijft een onderzoek naar de drukinvloed op de copolymerisatie van etheen en vinylacetaat in *tert*-butanol. Ten behoeve van het huidige en het toekomstige onderzoek is de invloed van temperatuur en oplosmiddelsoort op de kinetiek, evenals de invloed van de druk op het fasegedrag, onderzocht.

De experimentele methoden berusten op veelvuldige kwantitatieve gaschromatografische analyse van de voedingssamenstelling.

Om de drukinvloed op de monomere reaktiviteitsverhoudingen (r-waarden) te bepalen is de "sandwich" methode ontwikkeld. Alle experimenten bestaan uit drie delen. Gedurende het eerste deel wordt de druk laag (35 kg/cm^2, eerste deel) gehouden. Aan het einde van dit deel wordt de druk snel tot de gewenste hoge druk waarde (600 kg/cm^2, tweede deel) opgevoerd. Aan het einde van dit hoge druk deel wordt de druk snel verlaagd en de reaktie wordt in dit laatste deel bij lage druk (35 kg/cm^2, derde deel) voortgezet. Gedurende de eerste en de laatste delen wordt de voedingssamenstelling door veelvuldige monstername gevolgd. Uit deze gegevens kan de voedingssamenstelling aan het begin en het einde van het hoge druk deel nauwkeurig berekend worden door gebruik te maken van niet-lineaire kleinste kwadraten methoden die toegepast worden op geïntegreerde copolymerisatie vergelijkingen. Aldus levert elk experiment twee paar gegevens voor het hoge druk deel en twee series gegevens voor de lage druk delen. De gekombineerde gegevens van alle experimenten maken het mogelijk de r-waarden bij hoge en lage druk te bepalen met behulp van niet-lineaire kleinste kwadraten methoden. Toepassing van een statistische toets voor de

model "passing" toonde kleine systematische analyse fouten aan. Na korrektie van deze fouten zijn de volgende r-waarden gevonden

	62°C	34 kg/cm^2			62°C	600 kg/cm^2
$\hat{r}_e$ =	.750	st.d. .003		$\hat{r}_e$ =	.94	st.d. .04
$\hat{r}_v$ =	1.520	st.d. .004		$\hat{r}_v$ =	1.20	st.d. .04

Binnen de experimentele fout blijkt $\hat{r}_e * \hat{r}_v$ onafhankelijk van de druk te zijn. Dit is in overeenstemming met de hypothese dat reagerende monomeren en radikalen vaste bijdragen leveren aan het aktiveringsvolume. Deze bijdragen zijn onafhankelijk van de "transition state" waarin de reaktanten deelnemen. In dat geval is het verschil tussen de bijdragen van de monomeren

$$\boxed{\Delta V_e^{\#} - \Delta V_v^{\#} = -\ 11.6\ \text{cm}^3/\text{mole} \quad \text{st.d.} \quad 1.4}$$

Bovengenoemde hypothese kan de basis vormen voor een "monomeer aktiveringsvolume schema". Dit schema voorspelt de drukinvloed op de copolymerisatie van twee monomeren als de drukinvloed op de copolymerisatie van elk monomeer met een derde monomeer experimenteel bekend is. Dit kan ook een waardevolle hypothese zijn voor andere reakties dan polymerisatie reakties.

Het onderzoek naar de temperatuurinvloed op de r-waarden leverde gegevens op die overeenstemmen met het Alfrey model. De verschillen tussen de aktiveringsenthalpieën en entropieën van de propagatie stappen zijn

$\Delta H_{ee}^{\#} - \Delta H_{ev}^{\#}$ =	2039	cal/mole	st.d.	180
$\Delta H_{vv}^{\#} - \Delta H_{ve}^{\#}$ =	- 869	cal/mole	st.d.	125
$\Delta S_{ee}^{\#} - \Delta S_{ev}^{\#}$ =	5.49	cal/mole °C	st.d.	.55
$\Delta S_{vv}^{\#} - \Delta S_{ve}^{\#}$ =	- 1.77	cal/mole °C	st.d.	.40

Het onderschrift ev bijvoorbeeld verwijst naar de propagatie stap van het radikaal e met het monomeer v.

Tengevolge van toegenomen "chain transfer" door het oplosmiddel leidde het gebruik van *iso*-propanol in plaats van *tert*-butanol tot lagere molekulairgewichten van de copolymere produkten. Daardoor zijn de experimentele gegevens niet geheel in overeenstemming met het Alfrey model. De afwijkingen in de *r*-waarden die uit deze gegevens geschat zijn, zijn verklaard.

Daarnaast is een nieuw monstername ventiel (electromagnetisch naaldventiel) beschreven dat geschikt is voor rechtstreekse monstername uit hoge druk systemen. Dit ventiel verkeert echter nog in het ontwikkelingsstadium. De huidige resultaten vertonen wat grotere systematische afwijkingen dan die van de "sandwich" methode.

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LEVENSBERICHT

De schrijver van dit proefschrift werd op 27 juni 1943 te Amersfoort geboren. Hij genoot zijn middelbare schoolopleiding aan de Gooise H.B.S. te Bussum en het Gemeentelijke Lyceum te Eindhoven alwaar hij in 1961 het einddiploma H.B.S.-B behaalde. In dat jaar begon hij zijn studie aan de Technische Hogeschool te Eindhoven waar hij in 1969 na een afstudeerperiode bij prof. dr. D. Heikens zijn ingenieursdiploma verwierf. Sindsdien is hij als wetenschappelijk medewerker werkzaam in de sektie Kunststoftechnologie van de groep Chemische Technologie, tot 1972 in dienst van Z.W.O., momenteel in dienst van de Technische Hogeschool Eindhoven.

STELLINGEN

1 Hoewel een statistische "optimal design" studie voor een proefopzet zinvol is, moeten de resultaten hiervan met voorzichtigheid geïnterpreteerd worden, omdat deze niet noodzakelijkerwijze in overeenstemming zijn met de oorspronkelijke doelstelling van de onderzoeker.

W.J. Hill, W.G. Hunter and D.W. Wichern,
Technometrics, 10 (1968) 145.

2 Voor reactie-kinetische modelfuncties, die meer dan twee of drie parameters bevatten, verdient het aanbeveling de differentiële vorm in plaats van de geïntegreerde vorm met behulp van niet-lineaire methoden der kleinste kwadraten aan de waarnemingen te toetsen.

3 Als reactie-kinetische modelfuncties door middel van het meten van relatieve consumpties getoetst worden en de termen in de reactiesnelheidsvergelijkingen van dezelfde orde zijn mag de druk en/of het volume tijdens het experiment met behulp van een inert oplosmiddel constant gehouden worden.

4 Voor de gaschromatografische karakterizering naar samenstelling en structuur van polymeren en polymeermengsels is de thermische fragmentatiemethode te prefereren boven de fotolytische.

R.S. Juvet, Jr., J.L.S. Smith and Kwang-Pang Li,
Anal. Chem., 44 (1972) 49.
Encyclopedia of Polymer Science and Technology,
4 (1966) 682, Interscience Publishers,
New York.

5 In beschouwingen aangaande de relatie tussen aftastkrachten en aftastvervorming, tijdens het weergeven van grammofoonplaten, dienen de frequentie afhankelijke viscoelastische eigenschappen van de kunststoffen waaruit de platen vervaardigd zijn betrokken te worden.

H.L. Han, *Disk*, 55 (1971) 331.

6 Bij de technische specificatie van pick-up elementen ontbreekt ten onrechte vaak de tipmassa.

H.L. Han, *Disk*, 48 (1971) 761.

7 Het gebruik van een kunststof, die onder invloed van het milieu ontleedt, moet ontraden worden zolang de uitwerking van de vrijkomende ontledingsprodukten op het milieu niet bekend is.

N.R.C. 19-7-1972.
Chem. Eng. News, 49 (1971) 10.

Eindhoven, 24 november 1972 F. de Kok