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THE COPOLYMERIZATION OF ETHYLENE AND VINYLACETATE AT LOW PRESSURE

DETERMINATION OF THE KINETICS BY SEQUENTIAL SAMPLING

A.L. GERMAN

THE COPOLYMERIZATION OF ETHYLENE AND VINYLACETATE AT LOW PRESSURE

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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. A. A. TH. M. VAN TRIER, HOOGLERAAR IN DE AFDELING DER ELEKTROTECHNIEK, VOOR EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP DINSDAG 1 DECEMBER 1970 DES NAMIDDAGS TE 4 UUR

DOOR

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DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOR

PROF. DR. D. HEIKENS

Aan mijn ouders
Aan mijn vrouw

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CHAPTER 1

INTRODUCTION

1.1 SHORT HISTORICAL SURVEY

The copolymerization of ethylene with vinylacetate and other vinyl monomers under the condition of high pressure was documented in the patent literature as early as 1938 (ref. 1). The copolymers were prepared under the influence of free-radical initiators at temperatures varying from 50-250°C. It was believed that relatively high pressures (1000-2500 kgf/cm^2) were necessary in order to obtain high molecular weight copolymers over a wide composition range. Although these copolymers were interesting from the scientific point of view and several composition regions showed attractive properties, no attempts were made to describe the copolymerization behaviour and the products were prepared in a merely empirical way.

In spite of the fact that in 1944 (refs. 2, 3) models were reported for the description of copolymerization reactions in general, it lasted until the period 1962-1967 before some more attention was paid to the copolymerization reaction of ethylene with vinylacetate (refs. 4-8). It was recognized, by that time, that the condition of high pressure (1000-2500 kgf/cm^2) applied to some extent only to the bulk copolymerization, in the gas phase, of ethylene with a small quantity of vinylacetate. In case of solution copolymerization in the liquid phase, pressure played a less important part, and some of the experiments reported during the period mentioned were carried out in the liquid phase at pressures varying from 400-1000 kgf/cm^2 (refs. 5, 6, 8).

The growing interest might be explained partly because the copolymers of ethylene and vinylacetate became commercially interesting products and partly because several investigators were of the opinion that ethylene instead of styrene would be the most reasonable reference monomer in the *Q-e* scheme, i.e. a semi-quantitative scheme of correlation in which the individual monomer reactivities in copolymerization are described with respect to one chosen reference monomer.

However, the published results concerning the relation between the monomer feed and the copolymer composition at various reaction conditions, expressed in terms of the monomer reactivity ratios, appeared to be contradictory and unsurveyable. Besides, the copolymerization of ethylene with vinylacetate was mostly presupposed to obey the Alfrey model and the consistency of the experimental data with the proposed model was not sufficiently proved.

All in all the reported values raised substantial doubts with regard to their reliability and they probably suffered from two important sources of uncertainty:

- primarily, the doubts connected specifically with the system ethylene-vinylacetate and the experimental procedure, such as the inaccuracy in the determination of the monomer feed composition caused by the gaseous state of one of the monomers, the thick-walled autoclaves preventing observation of the phase behaviour in the vessel, and the error in the compositional analysis of the copolymer product;
- secondly, the inaccuracy involved in the method commonly used to determine the reactivity ratios; a method dealing with a number of low-conversion kinetic experiments, starting from different monomer feed compositions, of which only the initial and final conditions were entered into the model description in order to calculate the monomer reactivity ratios and to check the adequacy of the model.

1.2 CONCLUSIONS

- Neither in the study of the kinetics of copolymerization reactions under more complicated conditions (gaseous monomers, pressure, two-phase systems, etc.), nor in the accuracy of the determination of the monomer reactivity ratios and in model testing, is any progress to be expected unless advanced experimental methods allow continuous measurement of the monomer feed composition during each kinetic series. Only such measurements provide the complementary information on what happens exactly between the beginning and the end of the reaction, whereas the classical methods only supply data, often doubtful, about the initial and the final condition of a low-conversion copolymerization experiment.

- The study of the copolymerization reaction of ethylene with vinylacetate needs a straightforward approach.

1.3 AIM OF THE PRESENT INVESTIGATION

The aim of the investigation is:

- The design and evaluation of an improved and generally applicable experimental method, based on frequent measurement of the monomer feed composition during each kinetic series, in behalf of a detailed study of copolymerization reactions in which gaseous and/or liquid monomers play a part at pressures up to 40 kgf/cm^2 (see chapters 4, 5).
- The application of this method to the free-radical copolymerization of ethylene and vinylacetate in a liquid reaction phase at 62°C and a pressure of 35 kgf/cm^2 (see chapter 6). Since the reactivity ratios reported in the literature arouse doubts as for the homogeneity of the reaction mixture, a study of the phase behaviour is a necessity (see chapter 6).
- A precise determination of the monomer reactivity ratios of the system ethylene-vinylacetate under the conditions mentioned (see chapter 7).
- A model test, elucidating the question whether or not the copolymerization of ethylene and vinylacetate under the quoted conditions can be adequately described by the Alfrey model (see chapter 7).

The realization of the above aims would fill up a gap in the literature about ethylene-vinylacetate copolymerization and would yield additionally a new and generally applicable experimental research procedure, being useful in all polymerization or copolymerization studies.

On the other hand it would provide a basis for further research on the influence of pressure on the reaction kinetics of the copolymerization reaction of ethylene and vinylacetate. Such an investigation requires primarily the knowledge of the copolymerization behaviour at low pressure (preferably at atmospheric pressure, but some pressure is needed to introduce a sufficiently large amount of ethylene into the reaction mixture).

1.4 SOME PROPERTIES OF ETHYLENE-VINYLACETATE (EVA) COPOLYMERS

The physical and mechanical properties of EVA copolymers are mainly determined by their mean composition, the sequence distribution and the intermolecular homogeneity. As for the last two influences, the copolymers prepared during this investigation are supposed to differ in some measure from the commercial products. This indicates that one should be on one's guard against considering a copolymer of given overall composition and molecular weight as a well-defined material. The investigation of the physical and mechanical properties of the products obtained is, however, beyond the scope of this thesis. Only the general tendencies in the properties, as for example summarized in (refs. 9, 10) will be given briefly.

The crystallinity of the copolymers decreases and the permeability to water vapour increases with increasing vinylacetate content.

Copolymers containing up to 10 mole % vinylacetate have the character of low-density polyethylene but are more flexible and more extensible. Over the range 20-30 mole % vinylacetate rubbery products are obtained, showing low tensile strengths and high elongations; these copolymers can be cross-linked to improve the elastomeric properties. The copolymers become softer at higher ranges and at 50-60 mole % vinylacetate they are waxy and tacky at room temperature and have very low tensile strengths. Copolymers containing more than 80 mole % vinylacetate become stiffer and have a higher tensile strength.

The solubility of the copolymers also changes with the composition. Since the crystallinity of polyethylene is already destroyed by small amounts of vinylacetate in the polymer chains, copolymers containing about 5 mole % vinylacetate become soluble in toluene and other aromatic or chlorinated hydrocarbons. At 40 mole % vinylacetate the copolymer is still soluble in toluene and insoluble in ethanol. Copolymers containing 50-80 mole % vinylacetate are soluble in ethanol-toluene mixtures, and above 85 mole % vinylacetate the copolymers are soluble in ethanol, whereas toluene becomes a relatively poor solvent.

EVA copolymers are used as modifiers in waxes (e.g. for paper coating), in hot-melt adhesives (e.g. as instant-setting adhesive on ultrafast packaging or fabricating machines), and in paints. In addition, the copolymers are used for the processing, following the usual moulding and extrusion techniques, of a large number of widely different articles requiring low-temperature flexibility.

Besides, the EVA copolymers can be partially or completely hydrolyzed, yielding the terpolymer poly-{ethylene-vinylalcohol (-vinylacetate)}. Varying the most essential parameters, copolymer composition and percentage of hydrolysis, a variety of quite different specifications can be met. The terpolymers are preferred in many uses, such as fabric coatings, safety glass interlayers and fuel cell liners. Fibres from the completely or partially hydrolyzed EVA copolymers of high vinylacetate content can compete with the polyvinylalcohol fibres; an advantage over polyvinylalcohol is the insolubility in water of the fibres made from hydrolyzed EVA copolymers. Moreover, the latter can be melt-spun without decomposition.

REFERENCES

1 M.W. Perrin et al., *B.P.* 497,643 (1938) and *U.S.P.* 2,200,429 (1940).

2 T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, 12 (1944) 205.

3 F.R. Mayo and F.M. Lewis, *J. Am. Chem. Soc.*, 66 (1944) 1594.

4 N.L. Zutty and R.D. Burkhart, *Advan. Chem. Ser.*, 34 (1962) 52.

5 R.D. Burkhart and N.L. Zutty, *J. Polymer Sci. A*, 1 (1963) 1137.

6 R.A. Terteryan, A.I. Dintses and M.V. Rysakow, *Neftekhimiya*, 3 (1963) 719.

7 F.E. Brown and G.E. Ham, *J. Polymer Sci. A*, 2 (1964) 3623.

8 B. Erussalimsky, N. Tumarkin, F. Duntoff, S. Lyubetzky and A. Goldenberg, *Makromol. Chem.*, 104 (1967) 288.

9 E.T. Pieski, in *Polythene - the Technology and Uses of Ethylene Polymers*, (1960) chapter 13, Interscience Publishers, New York.

10 E.M. Fettes, in *Crystalline Olefin Polymers part II*, (1964) chapter 6B, Interscience Publishers, New York.

CHAPTER 2

THE FREE-RADICAL COPOLYMERIZATION 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). The basic equation for this model will be derived more generally than did these investigators.

2.1.1 DERIVATION ACCORDING TO MAYO, LEWIS, ALFREY AND GOLDFINGER

Mayo and Lewis (ref. 1) and Alfrey and Goldfinger (ref. 2) derived the copolymerization equation on the following main conditions:

- Initiation and termination steps play no part and only propagation steps are considered; this means a sufficiently high molecular weight.
- The steady-state assumption; this means each type of free radical is maintained at a certain concentration.
- Using $-dc_a/dt = k\ c_a c_b$, where c_a and c_b are monomer concentrations,
  $-dc_a/dt$ = rate of consumption of monomer "a" and
  k = second order rate constant,
  the implicit assumption of constant reaction volume was made.

By definition, the reaction rate is (ref. 3):

$$r = -\frac{1}{V}\frac{dn}{dt}$$

where r = reaction rate in mol/(unit volume x unit time)
V = reaction volume
n = number of moles
t = time

For a second order bimolecular reaction:

$$r = -\frac{1}{V}\frac{dn_a}{dt} = k\, c_a c_b$$

and

$$-\frac{dn_a}{dt} = k\, V\, c_a c_b = k\, n_a c_b$$

From direct kinetic considerations it can also be proved that the rate of disappearance of "a" has to be proportional to the number of molecules "a" and to the probability of finding a molecule "b" within a certain volume around "a", that is to say to the concentration of "b".

Thus, by supposing $-dc_a/dt = k\, c_a c_b$, V is assumed to be a constant. In the following it will be proved that the latter assumption is an unnecessary condition. The copolymerization equation has a more general validity, if concentrations are replaced by numbers of moles.

Assuming that the penultimate unit will not influence the addition of monomers to the growing chain and that the rate constants will not depend on the chain length, only four propagation reactions have to be considered:

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

It follows for the rate of consumption of the monomers that:

$$-\frac{dn_a}{dt} = k_{aa}\, n_a\, [a\cdot] + k_{ba}\, n_a\, [b\cdot] \tag{2-1}$$

$$-\frac{dn_b}{dt} = k_{ab}\, n_b\, [a\cdot] + k_{bb}\, n_b\, [b\cdot] \qquad (2\text{-}2)$$

The steady-state assumption for the free-radical chain ends gives:

$$k_{ab}\, n_b\, [a\cdot] = k_{ba}\, n_a\, [b\cdot] \quad \text{or} \quad [a\cdot] = \frac{k_{ba}\, n_a}{k_{ab}\, n_b}\, [b\cdot] \qquad (2\text{-}3)$$

The composition of the instantaneously formed copolymer is:

$$\frac{-\dfrac{dn_a}{dt}}{-\dfrac{dn_b}{dt}} = \frac{dn_a}{dn_b} \qquad (2\text{-}4)$$

And thus from (2-1), (2-2), (2-3) and (2-4):

$$\frac{dn_a}{dn_b} = \frac{r_a \dfrac{n_a}{n_b} + 1}{r_b \dfrac{n_b}{n_a} + 1} \qquad (2\text{-}5)$$

where $r_a = k_{aa}/k_{ab}$ and $r_b = k_{bb}/k_{ba}$ are the monomer reactivity ratios. The reactivity ratios indicate the preference exhibited by a certain radical at the end of the growing chain for a monomer unit of the same kind to a monomer unit of the other kind.

2.1.2 DERIVATION ACCORDING TO GOLDFINGER AND KANE

Goldfinger and Kane (ref. 4) derived the copolymerization equation in a very attractive way since they describe the sequence distribution in copolymerization.

Except for the steady-state assumption, their derivation is made under the same conditions as required by Mayo and

Lewis (ref. 1) and Alfrey and Goldfinger (ref. 2), inclusive of the implicit but again unnecessary condition of constant reaction volume. Their claim, however, to be able to avoid the steady-state assumption is of doubtful significance. The definition of the probabilities for the purpose of this derivation, already implies that only propagation steps are considered. The use of this definition is allowed if experiments are involved, in which initiation and termination steps are negligible with respect to the propagation steps, viz. yielding sufficiently high molecular weight products.

The chains formed during copolymerization can be considered as being composed of homogeneous sequences of the two different monomers:

........aaabbabbbaaaabbabaabb........

So the following probabilities may be defined:

p_{aa} is the probability of monomer "a" adding to radical "⁓a·"
p_{ab} is the probability of monomer "b" adding to radical "⁓a·"
p_{bb} is the probability of monomer "b" adding to radical "⁓b·"
p_{ba} is the probability of monomer "a" adding to radical "⁓b·"

Assuming that only propagation steps are involved, which means directly a steady state and high molecular weight, the following equations hold:

$$p_{aa} + p_{ab} = 1$$

and

$$p_{bb} + p_{ba} = 1$$

Every sequence of "a's" is bounded by "b's".

Now the "molefraction" of sequences of n "a's" built in a chain by propagation is equal to the probability of a given "ba·" pair to react with n-1 monomer molecules "a" in succession, followed by a reaction with one molecule "b". This probability and thus the "molefraction" is:

$$N_n = p_{aa}^{\,n-1}\, p_{ab} = p_{aa}^{\,n-1}\,(1 - p_{aa}) \qquad (2\text{-}6)$$

The number-average sequence length of "a's", started and ended by propagation reaction, is:

$$\bar{n}_a = \frac{\sum_{n=1}^{\infty} n\, N_n}{\sum_{n=1}^{\infty} N_n} = \frac{\sum_{n=1}^{\infty} n\, p_{aa}^{\,n-1}\,(1 - p_{aa})}{1}$$

$$= \frac{1 - p_{aa}}{p_{aa}} \sum_{n=1}^{\infty} n\, p_{aa}^{\,n}$$

$$= 1 + p_{aa} + p_{aa}^{2} + p_{aa}^{3} + \ldots\ldots$$

With $p_{aa} < 1$ this geometrical progression leads to:

$$\bar{n}_a = \frac{1}{1 - p_{aa}} = \frac{1}{p_{ab}} \tag{2-7}$$

correspondingly:

$$\bar{n}_b = \frac{1}{1 - p_{bb}} = \frac{1}{p_{ba}} \tag{2-8}$$

and consequently:

$$\frac{\bar{n}_a}{\bar{n}_b} = \frac{p_{ba}}{p_{ab}} \tag{2-9}$$

The probabilities p_{ba} and p_{ab} can be expressed as follows, where the reaction volume is not necessarily constant:

$$p_{ba} = \frac{k_{ba}\, n_a}{k_{ba}\, n_a + k_{bb}\, n_b} = \frac{1}{1 + r_b \dfrac{n_b}{n_a}} \tag{2-10}$$

$$p_{ab} = \frac{k_{ab}\, n_b}{k_{aa}\, n_a + k_{ab}\, n_b} = \frac{1}{1 + r_a \dfrac{n_a}{n_b}} \tag{2-11}$$

During a batch process the value of p changes continuously. The instantaneous values of p, however, rule the average sequence length of the copolymer formed by propagation at the same moment.

Since the numbers of "a" and "b" sequences formed by propagation reactions are equal, which is mathematically equivalent to the steady-state assumption (2-3), it follows that $\bar{n}_a/\bar{n}_b$ by propagation is the ratio of "a" and "b" occurring in the instantaneously formed copolymer. Thus,

$$\frac{\bar{n}_a}{\bar{n}_b} = \frac{-\frac{dn_a}{dt}}{-\frac{dn_b}{dt}} = \frac{dn_a}{dn_b} \qquad (2\text{-}12)$$

= ratio of the instantaneous rates of consumption of the monomers by propagation.

From equations (2-9), (2-10), (2-11) and (2-12) follows

$$\frac{dn_a}{dn_b} = \frac{r_a \frac{n_a}{n_b} + 1}{r_b \frac{n_b}{n_a} + 1}$$

where the well-known copolymerization equation (2-5) appears again.

After integration of this equation (see 2.3), the competency of this model to describe the copolymerization reaction of ethylene with vinylacetate will be investigated and the reactivity ratios will be determined (see chapters 7 and 8).

2.2 EXTENSION OF THE MODEL FOR FREE-RADICAL VINYL COPOLYMERIZATION

One of the assumptions made in the derivation of the copolymerization equation (2-5) is that only the final unit of the growing-chain end will influence the addition of monomers. If only the penultimate unit is taken into account, already eight propagation steps have to be considered and four reactivity ratios are involved. The derivation of the expanded copolymerization equation is given by Ham (ref. 5).

Brown and Ham (ref. 6) report influence of the penultimate and the pen-penultimate unit in the copolymerization of ethylene-methylacrylate, ethylene-methylmethacrylate, and methylacrylate-methylmethacrylate. No such effects have been found, however, for ethylene-vinylacetate copolymerization at 840 kgf/cm^2 and 150°C (ref. 6).

Another possible deviation from the conventional copolymerization equation may occur if a considerable amount of "head-to-head" units is formed. Homopolymerization of vinyl monomers gives polymers with 98-100% "head-to-tail" structure because of the greater thermodynamic advantage of its accompanying propagation step. According to Flory and Leutner (ref. 7) the fraction of "head-to-head" addition at 62°C can be calculated as 1.5% of the total number of additions in the case of vinylacetate polymerization. In copolymerization, conditions are more favourable to forming "head-to-head" units if e.g. ethylene is involved, since steric inhibitions and polarity factors restricting the possibility of anomalous addition in homopolymerization, partly cease to exist.

Anomalous addition reactions in ethylene-vinylacetate copolymerization are considered by Lyubetzky et al. (refs. 8, 9). However, in their derivation of an expanded copolymerization equation taking into account anomalous additions, some assumptions and approximations are made on dubious grounds and unfortunately the equation contains an error in the published form (ref. 8). Although the results of the present paper do not indicate the necessity of application (see 7.5) of this expanded equation, it seems worthwile to give the correct derivation.

The occurrence of anomalous additions can generally be considered as a special case of three-component terpolymerization, where the third component (c) is the anomalously added second component (b). Considering all terpolymer chains, four possibilities seem to exist in which an "a" sequence can be bounded:

ba......a......ab
ba......a......ac
ca......a......ab
ca......a......ac

If only propagation steps are considered (which means again high molecular weight and steady state for the radicals), it can be seen that the number of sequence-starting transitions equals the number of sequence-ending transitions. An "a" sequence can be started by either a "ba" or a "ca" transition and be ended by an "ab" or an "ac" transition.

For instance, according to the given definition p_{ba} is equal to the probability of monomer "a" adding to radical "$\sim b\cdot$", which is equivalent to saying that p_{ba} is the fraction of the "b" units present in the terpolymer, which are followed by an "a" unit. If A, B and C are the absolute amounts of "a", "b" and "c" present in the terpolymer, respectively, the absolute amount of for example "ba" transitions is Bp_{ba} and consequently:

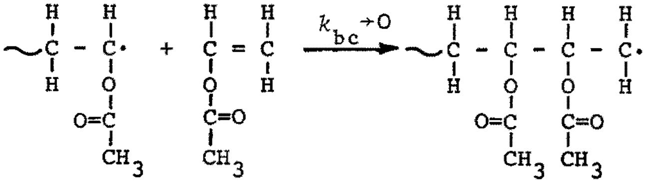
$$Bp_{ba} + Cp_{ca} = Ap_{ab} + Ap_{ac} \quad \text{for "a" sequences} \qquad (2\text{-}13)$$

similarly $$Ap_{ab} + Cp_{cb} = Bp_{ba} + Bp_{bc} \quad \text{for "b" sequences} \qquad (2\text{-}14)$$

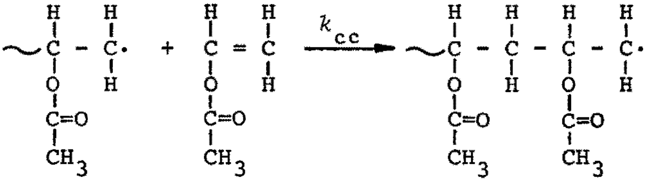
and $$Ap_{ac} + Bp_{bc} = Cp_{ca} + Cp_{cb} \quad \text{for "c" sequences} \qquad (2\text{-}15)$$

Now Lyubetzky et al. (refs. 8, 9) made the following assumptions (expressed in the nomenclature used here) for ethylene (a) - vinylacetate "head-to-tail" (b) - vinylacetate "head-to-head" (c):
$p_{bc} = 0$, and $p_{cc} = 0$ or $p_{ca} + p_{cb} = 1$.

$p_{bc} = 0$ means that a vinylacetate chain end will not add anomalously a vinylacetate unit:



This may seem a reasonable assumption, since according to (ref. 7) only 1.5% of the propagation steps in homopolymerization of vinylacetate at 62°C leads to anomalous addition. Goff, Zhulin and Gonikberg (ref. 10) found that an increase of pressure from atmospheric to 6000 kgf/cm^2 during homopolymerization of vinylacetate at 40°C leads to a *relative* increase of 22% in anomalous "head-to-head" additions. But even then the assumption $p_{bc} = 0$ seems quite acceptable. On the other hand $p_{cc} = 0$ means that an anomalous addition of vinylacetate will never be followed by another anomalous addition. For the time being no reasonable grounds are available to give sense to this statement, the more so as this addition is not restricted by steric hindrance:



For this reason only the assumption $p_{bc} = 0$ will be made in the following derivation.

From equations (2-13), (2-14) and (2-15) can be derived:

$$\frac{A}{B + C} = \frac{p_{ba}\ (p_{ca} + p_{cb})}{p_{ab}\ (p_{ca} + p_{cb}) + p_{ac}\ (p_{cb} + p_{ba})} \qquad (2\text{-}16)$$

After the definition for p_{ba}:

$$p_{ba} = \frac{k_{ba}\ n_a}{k_{ba}\ n_a + k_{bb}\ n_b + k_{bc}\ n_c}$$

and analogous expressions for p_{ca}, p_{cb}, p_{ab} and p_{ac}, equation (2-16) takes the form:

$$\frac{dn_a}{dn_b} = F\,\frac{r_a + \frac{1}{F}(m + 1)}{\left(r_b/F\right)\left(1 + \frac{mr_c}{F+r_c}\right) + 1 + m\left(1 + \frac{r_c + r_c'}{F+r_c}\right)} \tag{2-17}$$

where

$$\begin{array}{llll} \frac{dn_a}{dn_b} = \frac{A}{B + C} & & \frac{k_{cc}}{k_{ca}} = r_c' \\ \frac{k_{aa}}{k_{ab}} = r_a & & \frac{k_{ac}}{k_{ab}} = m \\ \frac{k_{bb}}{k_{ba}} = r_b & & n_b = n_c \\ \frac{k_{cb}}{k_{ca}} = r_c & & \frac{n_a}{n_b} = F \end{array}$$

When $m = 0$ equation (2-17) reduces to the conventional copolymerization equation.

If penultimate effects occur or anomalous addition takes place, the r-values calculated from the conventional copolymerization equation should be dependent on the initial monomer feed composition. It will become evident that the results of this investigation do not necessitate the use of extended models for the description of ethylene-vinylacetate copolymerization.

2.3 INTEGRATION OF THE COPOLYMERIZATION EQUATION

The copolymerization equation (2-5) can be integrated, yielding an exact relationship between the monomer feed composition and the degree of conversion. Equation (2-5) can be rearranged to:

$$\frac{d\left(\frac{n_a}{n_b}\right)}{df_b} = \frac{1}{(100 - f_b)}\left(\frac{n_a}{n_b} - \frac{r_a\frac{n_a}{n_b} + 1}{r_b\frac{n_b}{n_a} + 1}\right)$$

with the conversion based on monomer "b" defined as $f_b = 100\{1 - n_b/(n_b)_o\}\%$ and $(n_b)_o$ being the initial quantity of moles in the reactor.

Integration between the initial coordinates $(f_b)_o = 0$ and $(n_a/n_b)_o$ and the coordinates at the end of the reaction $(f_b)_e$ and $(n_a/n_b)_e$, yields:

$$\frac{r_b}{r_b - 1}\ln\frac{q_e(R + q_o)}{q_o(R + q_e)} + \frac{1}{1 - r_a}\ln\frac{q_e + R}{q_o + R} + \ln\frac{100 - (f_b)_e}{100} = 0$$

under the constraints $r_a \neq 1$ and $r_b \neq 1$

where $q_o = \left(\frac{n_a}{n_b}\right)_o$

$q_e = \left(\frac{n_a}{n_b}\right)_e$ and $R = \frac{r_b - 1}{1 - r_a}$

For purposes of calculating the r-values (see chapter 7) this equation is rearranged to:

$$(f_b)_e - 100\left\{1 - \left(\frac{q_e}{q_o}\right)^{-x_2-1}\left(\frac{x_2\,q_e - x_1}{x_2\,q_o - x_1}\right)^{x_1+x_2+1}\right\} = 0 \qquad (2\text{-}18)$$

with $x_1 = 1/(r_a-1)$, $x_2 = 1/(r_b-1)$, and consequently $x_1/x_2 = -R$.

Except for the arrangements made in connection with the specific parameters arising from the experiments described in this thesis, equation (2-18) corresponds with integrated forms derived by other investigators (refs. 1, 11, 12, 13).

2.4 THE SIGNIFICANCE OF THE MONOMER REACTIVITY RATIOS

The monomer reactivity ratios as they appear in the copolymerization equation are defined as follows:

$$r_a = \frac{k_{aa}}{k_{ab}} \quad \text{and} \quad r_b = \frac{k_{bb}}{k_{ba}}$$

The reactivity ratios indicate the preference of a certain chain radical to add a monomer unit of the same kind over a monomer unit of the other kind.

Considering the r-values, two types of copolymerization processes can be distinguished (see Fig. 2-1):

(1) A copolymer is "ideal" if $r_a = 1/r_b$ or $r_a r_b = 1$, this means each of the two radicals exhibits the same preference of adding one of the monomers over adding the other; the two types of unit are arranged at random along the chain in relative amounts determined by the composition of the feed and the relative activities of the two monomers. The copolymerization equation reduces to: $dn_a/dn_b = r_a(n_a/n_b)$.

(2) A copolymer is "alternating" if $r_a = r_b = 0$. Each radical prefers to add exclusively the other monomer. The monomers alternate regularly along the chain regardless of the monomer feed composition, and consequently: $dn_a/dn_b = 1$.

A third possibility might exist if each radical prefers to add its own monomer; this means $r_a > 1$ as well as $r_b > 1$. In the extreme case, this would result in simultaneous homopolymerization. This boundary case has so far not been experimentally observed with any known pair of monomers. A slight tendency towards homopolymerization, however, appearing from values for $r_a r_b$ between 1.0 and 1.5, is found to exist for several monomer pairs (ref. 14).

In most cases copolymerization behaviour for monosubstituted vinyl monomers lies between the "ideal" and the "alternating" systems, with $0 < r_a r_b < 1$ (ref. 14).

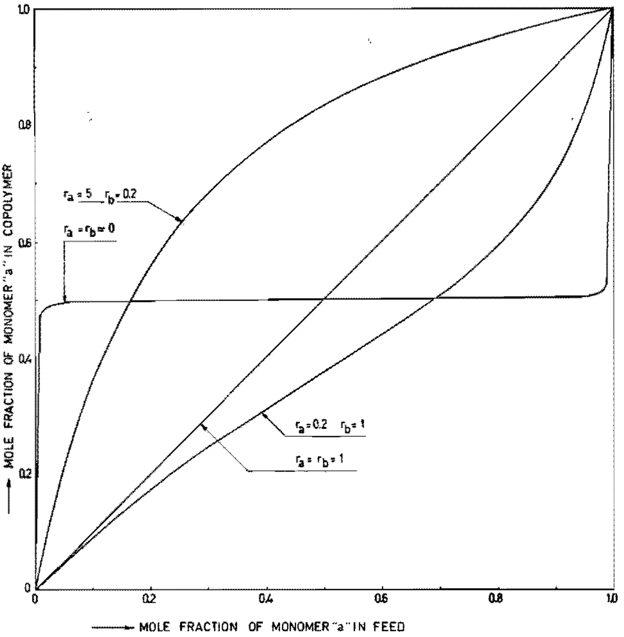


Fig. 2-1 Examples of the theoretical relationship between the monomer feed composition and the composition of the instantaneously formed copolymer for various values of r_a and r_b

2.5 THE *Q*-*e* SCHEME

The *r*-values, as evaluated from experiments, describe the kinetics of copolymerization for a system of two monomers, and consequently the results scarcely allow any predictions for other systems. That is the reason why several investigators (refs. 15, 16) made an attempt to characterize the monomer combinations by *monomer* parameters rather than by *system* parameters.

A generally accepted concept is that the monomer reactivity is governed by the following factors (ref. 17):

- sterical factors,
- conjugation of the double bond with unsaturated side groups, and
- the polarity of the double bond.

Alfrey and Price have set up a scheme of correlation (ref. 16), the *Q*-*e* scheme, in which monomer reactivity is described in a general and at least semi-quantitative way. Making an attempt to find a quantitative correlation between reactivity and polarity, they give an approximation of the propagation rate constants in the form:

$$k_{12} = P_1 Q_2 \exp(-\, e_1\, e_2) \ ,$$

where sterical factors are not taken into account. Although a certain similarity has been shown (refs. 18, 19, 20) with the Hammett equation (ref. 21) and the Hammett-Taft equation (ref. 22), the *Q*-*e* scheme is generally considered an empirical correlation.

P_1 = a constant connected with the specific reactivity of the radical 1 in terms of stabilization by resonance.
Q_2 = the reactivity of monomer 2 in terms of stabilization by resonance.
e_1 = proportional to the "charge" on the end group of radical 1.
e_2 = proportional to the "charge" on the double bond of monomer 2.

Combination with $k_{11} = P_1 Q_1 \exp(-\, e_1^{\,2})$, where the assumption is made that the "charge" on the double bond of a monomer equals that on the end group of the radical of the same monomer, leads to:

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp[-\, e_1\ (e_1 - e_2)] \qquad (2\text{-}19)$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1} \exp[-\, e_2\ (e_2 - e_1)] \qquad (2\text{-}20)$$

and $$r_1 r_2 = \pi = \exp[-\,(e_1 - e_2)^2] \qquad (2\text{-}21)$$

The product of reactivity ratios $\pi = r_1 r_2$ is an excellent measure of the alternation tendency in vinyl copolymerization. From equation (2-21) it will be clear that, according to the theory concerning the Q-e scheme, π cannot exceed unity. Inspection of Young's (ref. 14) tabulation of reactivity ratios shows, however, that this is not confirmed by all experiments.

Wall (ref. 23) suggested that an oversimplification of the Q-e scheme might be met by assigning a different electronegativity to monomer (e_1) and radical (e_1^*), leading to:

$$\pi = r_1 r_2 = \exp[-(e_1 - e_2)(e_1^* - e_2^*)]$$

In applying this expression, π could only exceed unity if the difference between the electronegativity of the chain ends is opposite in sign to the difference in eletronegativity of the monomers. Only in the case when the monomers exhibit approximately equal electronegativities, might such a situation be expected. O'Driscoll et al. (ref. 24) have shown, however, that this condition is far from being satisfied for monomer pairs with $\pi = r_1 r_2 > 0.95$. Apparently values of $\pi > 1$ can be explained neither by the original Q-e scheme, nor by expanded versions where monomer and radical are allowed different electronegativities.

The zero point of the Q-e scale

Alfrey and Price (ref. 16) arbitrarily took styrene as a reference monomer and gave it the Q-value of unity and the e-value of -1. Using these values, the values of Q and e for several other monomers can be calculated by means of copolymerization experiments with styrene. Then the r-values for new combinations of monomers can be predicted.

The zero point of the Q-e scale for e, chosen by Alfrey and Price on rather arbitrary grounds, lies apparently slightly higher than the "best" value (ref. 15). Price (ref. 25) proposed to lower the zero point of the e scale by 0.2 and accepted $Q = 1.0$ and $e = -0.8$ as a new reference point for styrene.

Several research workers (refs. 14, 26, 27, 28) have confirmed the usefulness of the revised Q-e scheme and shown that this correlation accounts for their copolymerization data.

In 1963, Burkhart and Zutty (ref. 29) made an attempt to base the Q-e scheme on ethylene as a reference monomer, with $Q_e = 1.0$ and $e_e = 0$. According to the equations (2-19), (2-20) and (2-21), and with $Q_2 = Q_e$ and $e_2 = e_e$ this leads to:

$$r_1 = (Q_o)_1 \exp[-(e_o)_1^2] \tag{2-22}$$

$$r_2 = \frac{1}{(Q_o)_1} \tag{2-23}$$

and

$$r_1 r_2 = \exp[-(e_o)_1^2] \tag{2-24}$$

where the subscript of Q_o and e_o indicates that ethylene is taken as a reference monomer. The advantages of ethylene as a reference monomer are obvious:

- though the value of $e_e = 0$ for ethylene does not pretend to describe the actual charge on the double bond, the e_o values of other monomers will represent the polarity on the double bond induced by a certain substituent.
- Q_o only depends on $r_2 = k_{22}/k_{21}$ and requires no adjustment owing to differences in double bond polarity. For that reason Q_o is a more straightforward measure of monomer reactivity than Q.
- the extent of ideality of the copolymer is exclusively determined by the e_o-value of the comonomer.

Conclusions

The results of the present research will show that, at least at low pressures for the system ethylene-vinylacetate, $\pi = r_e r_v = 1.12$ exceeds unity to a considerable extent. Consequently, the Q-e scheme not being able to describe suchlike systems, it will not be applied during this investigation.

On the ground of the results of experiments on the copolymerization of ethylene with vinyl monomers published so far, it is not yet justified to choose ethylene as a reference monomer. The considerations that have led to this conclusion will be discussed in 2.6 .

2.6 DISCUSSION OF SOME IMPORTANT REACTION CONDITIONS IN CONNECTION WITH THE RESULTS OBTAINED BY OTHER INVESTIGATORS

2.6.1 INFLUENCE OF PRESSURE ON REACTION KINETICS

The copolymerization processes in which ethylene is involved are generally carried out at pressures of 400-2000 kgf/cm^2. Burkhart and Zutty (ref. 30) determined the influence of pressure on the copolymerization behaviour of the monomer pairs: styrene-acrylonitrile and methylmethacrylate-acrylonitrile. They note that the product r_1r_2 approximates unity at increasing pressure, which indicates that the copolymerization becomes more ideal. In terms of Q and e this means that Q-values are relatively independent of pressures up to 1000 kgf/cm^2, where the e-values depend on pressure and tend to become equal.

Despite the oversimplification of the Q-e scheme, where the e-value is described in terms of electrostatic attraction, the e-value probably describes the tendency to form the transition state. Since the activating volume (= volume transition state minus volume reactants) is pressure dependent (ref. 31), the e-value will be so too. The Q-value, however, describes the reactivity of the monomer in terms of stabilization by resonance. No effective deformation of electron configurations is believed to exist at pressures below 3000 kgf/cm^2 (ref. 32) and hence the conjugation of the double bond with unsaturated substituents will scarcely be influenced by pressure.

In addition to influencing reaction rate constants, pressure may cause solubility changes or phase separation.

Another effect of pressure may be diffusion controlled chemical reactions. At high pressures the viscosity of the reaction medium may be increased to a considerable extent (ref. 33). On account of an increase of the viscosity of the reaction medium, either caused by polymer formation or by high pressure, the mutual termination of growing chains may be diffusion controlled. The consequent increase in (co)polymerization rate, independent of the radical initiator, is called the gel effect or Trommsdorff effect (refs. 34, 35). Although the propagation steps in copolymerization will generally not be affected by the gel effect, there might be an influence in specific cases.

For the reasons mentioned it is not desirable to take ethylene as a reference monomer in the *Q-e* scheme based upon ethylene copolymerizations carried out at pressures of 1000 kgf/cm^2 (ref. 29). A general discussion about influence of pressure on copolymerization behaviour is given by Kinkel (ref. 36).

2.6.2 THE RESULTS OF COPOLYMERIZATION EXPERIMENTS WITH ETHYLENE AND VINYLACETATE CARRIED OUT BY OTHER INVESTIGATORS

Erussalimsky et al. (ref. 37) have determined the influence of pressure on the copolymerization behaviour of ethylene and vinylacetate; the results are listed in Table 2-1, together with data from other investigators.

Although the deviations of their results from other data cause doubts about the absolute reliability of these measurements, for the time being it seems reasonable not to exclude the existence of a noticeable influence of pressure.

Table 2-1 Literature concerning the copolymerization of ethylene and vinylacetate

sources	reference	r_e	r_v	$\pi = r_e r_v$	reaction conditions		
					temp. °C	pressure kgf/cm^2	solvent
Burkhart and Zutty	(ref.29)1963	1.07	1.08	1.16	90	1000	toluene
Terteryan et al.	(ref.38)1963	0.77	1.02	0.79	70	400	benzene
Terteryan et al.	(ref.38)1963	0.97	1.02	0.99	130	400	benzene
Brown and Ham	(ref. 6)1964	1.01	1	1	150	840	—
Erussalimsky et al.	(ref.37)1967	0.16	1.14	0.18	60	100	—
Erussalimsky et al.	(ref.37)1967	0.70	3.70	2.59	60	1200	—
This investigation	(chapter 7)	0.74	1.51	1.12	62	35	TBA

As Table 2-1 illustrates, many investigators have carried out copolymerization experiments of ethylene and vinylacetate, most of them at moderately high pressures. None of them, except the author of this thesis, has convinced himself by direct observation of the homogeneity of the reaction mixture (see 6.4), although this is a condition for the application of the Alfrey model describing the kinetics of radical copolymerization of vinyl monomers.

REFERENCES

1 F.R. Mayo and F.M. Lewis, *J. Am. Chem. Soc.*, 66 (1944) 1594.
2 T. Alfrey Jr. and G. Goldfinger, *J. Chem. Phys.*, 12 (1944) 205.
3 S.M. Walas, *Reaction kinetics for chemical engineers*, (1959) 5, MacGraw-Hill, New York.
4 G. Goldfinger and T. Kane, *J. Polymer Sci.*, 3 (1948) 462.
5 G.E. Ham, *Copolymerization*, (1964) 9, Interscience Publishers, New York.
6 F.E. Brown and G.E. Ham, *J. Polymer Sci. A*, 2 (1964) 3623.
7 P.J. Flory and F.S. Leutner, *J. Polymer Sci.*, 3 (1948) 880.
8 S. Lyubetzky, A. Goldenberg, F. Duntoff and B. Erussalimsky, *J. Polymer Sci. C*, 6 (1968) 109.
9 S.G. Lyubetzky, B.L. Erussalimsky and A.L. Goldenberg, *Dokl. Akad. Nauk SSSR*, 172 (1967) 1372.
10 A.L. Goff, V.M. Zhulin and M.G. Gonikberg, *Dokl. Akad. Nauk SSSR*, 176 (1967) 1302.
11 D.W. Behnken, *J. Polymer Sci. A*, 2 (1964) 645.
12 V.E. Meyer and G.G. Lowry, *J. Polymer Sci. A*, 3 (1965) 2843.
13 W. Ring, *Makromol. Chem.*, 101 (1967) 145.
14 L.J. Young, *J. Polymer Sci.*, 54 (1961) 411.
15 F.M. Lewis, F.R. Mayo and W.F. Hulse, *J. Am. Chem. Soc.*, 67 (1945) 1701.
16 T. Alfrey and C.C. Price, *J. Polymer Sci.*, 2 (1947) 101.
17 T. Alfrey, J.J. Bohrer and H. Mark, *Copolymerization* (1952) 45, Interscience Publishers, Inc., New York.

18 C. Walling, E.R. Briggs, K.B. Wolfstirn and F.R. Mayo, *J. Am. Chem. Soc.*, 70 (1948) 1537.

19 T.C. Schwan and C.C. Price, *J. Polymer Sci.*, 40 (1959) 457.

20 M.C. Shen, *J. Polymer Sci. B*, 1 (1963) 11.

21 L.P. Hammett, *Chem. Rev.*, 17 (1935) 125.

22 R.W. Taft Jr., *J. Phys. Chem.*, 64 (1960) 1805.

23 L.A. Wall, *J. Polymer Sci.*, 2 (1947) 542.

24 K.F. O'Driscoll, T. Higashimura and S. Okamura, *Makromol. Chem.*, 85 (1965) 178.

25 C.C. Price, *J. Polymer Sci.*, 3 (1948) 772.

26 B.R. Thompson and R.H. Raines, *J. Polymer Sci.*, 41 (1959) 265.

27 T. van der Hauw, *J. Polymer Sci. B*, 3 (1965) 715.

28 T. Ito, T. Otsu and M. Imoto, *J. Polymer Sci. B*, 4 (1966) 81.

29 R.D. Burkhart and N.L. Zutty, *J. Polymer Sci. A*, 1 (1963) 1137.

30 R.D. Burkhart and N.L. Zutty, *J. Polymer Sci.*, 57 (1962) 793.

31 K.E. Weale, *Chemical reactions at high pressures*, (1967) 136, E. & F.N. Spon Ltd., London.

32 E. Hunter, in *Polythene - the Technology and Uses of Ethylene Polymers*, (1960) chapter 3, Interscience Publishers, New York.

33 P.W. Bridgman, *Proc. Am. Acad. Arts. Sci.*, 61 (1926) 57.

34 R.F.W. Norrish and E.F. Brookman, *Proc. Roy. Soc. (London)*, A 171 (1939) 147.

35 E. Trommsdorff, H. Kohle and P. Lagally, *Makromol. Chem.*, 1 (1948) 169.

36 K. Kinkel, *Ber. Bunsenges. Physik. Chem.*, 70 (1966) 1030.

37 B. Erussalimsky, N. Tumarkin, F. Duntoff, S. Lyubetzky and A. Goldenberg, *Makromol. Chem.*, 104 (1967) 288.

38 R.A. Terteryan, A.I. Dintses and M.V. Rysakow, *Neftekhimiya*, 3 (1963) 719.

CHAPTER 3

SURVEY OF THE VARIOUS METHODS OF DETERMINING THE MONOMER REACTIVITY RATIOS

In the literature several methods are described for the determination of the monomer reactivity ratios. In this chapter the intersection method will be discussed, which is the procedure most frequently resorted to. It is to some extent related to the F.C.A.(procedure A) method (see 7.3), used in this investigation to calculate the r-values. Besides, a survey will be given of the other procedures to determine r-values.

3.1 THE INTERSECTION METHOD (ref. 1)

The copolymerization equation (2-5) can be rewritten as:

$$r_b = \frac{n_a}{n_b}\left\{\frac{dn_b}{dn_a}\left(1 + \frac{n_a}{n_b}r_a\right) - 1\right\}, \tag{3-1}$$

or $\quad r_b = A\,r_a + B \quad$ with $\quad A = \left(\frac{n_a}{n_b}\right)^2 \frac{dn_b}{dn_a}$

and $\quad B = \frac{n_a}{n_b}\left(\frac{dn_b}{dn_a} - 1\right)$

Generally the r-values are determined by carrying out at least two copolymerization experiments up to a low degree of conversion (approximately 10%), starting from different monomer feed compositions. Then the reaction is stopped, the copolymer isolated and its composition determined by analysis. The value of n_a/n_b at the *beginning* of the reaction is substituted in equation (3-1), and for dn_a/dn_b the *mean* copolymer composition is taken. This procedure is not correct since the composition of the monomer feed changes continuously during the reaction, and consequently so does the composition of the formed copolymer. The magnitude of the error depends on the degree of conversion, on the magnitude of the r-values and on the differences between the initial monomer feed compositions of the kinetic series concerned.

Besides this, a reliable determination of n_a/n_b at the beginning of the reaction may be very difficult, if gaseous monomers are involved. The proper isolation and analysis of the copolymer may also cause considerable errors.

Since r_b is a linear function of r_a, any experiment determines one straight line in the $r_a - r_b$ plane, with a slope dependent on the initial feed composition. These lines will generally not intersect in one single point but will define an area of significant intersection points, of which e.g. the centre of gravity is chosen as the best pair of r-values and of which the dimensions are characteristic of the experimental errors involved as well as of the ability of the usual copolymerization model to describe the experiments.

3.2 OTHER PROCEDURES TO DETERMINE r-VALUES

The linearization method (ref. 2)

Equation (3-1) can be rearranged to:

$$\frac{n_a}{n_b}\left(\frac{dn_b}{dn_a} - 1\right) = \left\{ -\left(\frac{n_a}{n_b}\right)^2 \frac{dn_b}{dn_a}\right\} r_a + r_b$$

For a series of experiments over a wide range of monomer feed compositions, $(n_a/n_b)(dn_b/dn_a - 1)$ is plotted versus $-(n_a/n_b)^2\, dn_b/dn_a$. The best fitting straight line is drawn through these points. The slope of the straight line is r_a and the intercept is r_b.

The approximation method (ref. 3)

The copolymerization equation (2-5) can be rearranged, showing the relationship between the mole fraction of monomer "a" in the monomer feed (x) and the mole fraction of monomer "a" in the instantaneously formed copolymer (y):

$$y = \frac{x^2 (r_a - 1) + x}{x^2 (r_a + r_b - 2) + 2x (1 - r_b) + r_b} \tag{3-2}$$

From this equation follows:

$$\left(\frac{dy}{dx}\right)_{x=0} = \frac{1}{r_b} \quad \text{and} \quad \left(\frac{dy}{dx}\right)_{x=1} = \frac{1}{r_a}$$

and at very low concentrations of monomer "a" and "b" respectively, an approximation of r_b and r_a is provided by:

$$r_b \simeq \left(\frac{x}{y}\right)_{x\to 0} \qquad r_a \simeq \left(\frac{x}{y}\right)_{x\to 1}$$

The main advantage of this method is that a quick approximation of r_b and r_a is obtained from two experiments. The limitations of the method are, however, numerous. In the first place extremely sensitive analytical methods are required for the determination of the very small quantities of monomer "a" or "b" in the copolymer. Secondly, the assumption is made that the experiments are described by the usual copolymerization equation, and any deviations from this model do not show up. Moreover, the extreme monomer feed compositions are in particular the regions where deviations from the assumed boundary conditions (see 2.1) could be expected.

The curve fitting method (ref. 4)

A number of experiments are carried out up to a low degree of conversion and the copolymers are isolated and compositionally analyzed. The initial mole fraction of monomer "a" in the monomer feed is plotted versus the mean mole fraction of monomer "a" in the copolymer. Arbitrarily chosen values of r_a and r_b are substituted in equation (3-2) and graphs are plotted of

y versus x. Using the trial and error method, those values of r_a and r_b are chosen that provide the curve which fits the points best.

This method requires extensive calculations, whereas a large number of experiments is needed to obtain a still subjective pair of r-values with unknown precision.

The spectral method (ref. 5)

Although primarily used for structural investigation of copolymers in terms of the monomer sequence distributions (refs. 5, 6, 7), high resolution NMR spectroscopy may be useful to estimate r-values in copolymerization.

In cases where the fractions of triads in a copolymer can be determined from NMR spectra, the number-average sequence lengths are found by:

$$\bar{n}_a = \frac{2}{1 + bab - aaa} \qquad \bar{n}_b = \frac{2}{1 + aba - bbb}$$

where e.g. aaa = the fraction of triads "aaa" in the copolymer, with $aaa + aab + baa + bab = 1$.
Combination with equations (2-7), (2-8), (2-10) and (2-11) yields:

$$\bar{n}_a = \frac{2}{1 + bab - aaa} = \frac{1}{p_{ab}} = 1 + r_a \frac{n_a}{n_b}$$

and $$\bar{n}_b = \frac{2}{1 + aba - bbb} = \frac{1}{p_{ba}} = 1 + r_b \frac{n_b}{n_a}$$

A series of experiments is carried out with different initial feed compositions up to a low degree of conversion. The products are isolated and $\bar{n}_a$ and $\bar{n}_b$ determined from NMR spectra. Plottings of $\bar{n}_a$ versus n_a/n_b and $\bar{n}_b$ versus n_b/n_a provide straight lines (if the usual model holds) with slopes r_a and r_b.

The typical disadvantages of this method are the non-universal applicability and the considerable error, about ± 5%

(ref. 7), in determining the fractions of triads. In addition, this method generally requires rather advanced (220 MHz) NMR techniques.

3.3 CONCLUSION

Although several authors have given computational perfections (refs. 8, 9, 10, 11) of the methods mentioned, all these procedures still have the following disadvantages in common:

- a All the methods in question are based on the fact that only the *initial* feed composition and the *mean* copolymer composition are experimentally accessible parameters. These parameters, derived from low-conversion experiments, are substituted in the differential form of the copolymerization equation (2-5), whereas the initial (instantaneous) monomer feed composition *should* be combined in the equation mentioned with the composition of the initially (instantaneously) formed copolymer.
- b Reliable determination of the initial feed composition may be very difficult, if gaseous monomers are involved.
- c The isolation of the copolymer, its purification and compositional analysis are potential sources of error and, moreover, time consuming and subjective procedures. No general method of compositional analysis can be given for all types of copolymers.
- d One copolymerization experiment provides only one single pair of data (monomer feed and copolymer composition).
- e The requirement of low conversion may cause the measured data to be considerably affected by contributions due to non-stationary phenomena occurring at the beginning of the reaction.

The significance of using the integrated form of the copolymerization equation (2-18) for high-conversion experiments has been recognized earlier (refs. 12, 8, 10, 11). As the only input data per experiment are, however, the initial feed composition and the final feed composition calculated from the mean copolymer composition, the disadvantages b, c and d still exist. Furthermore, the input data must be accurate to the order of ± 0.01% to allow sufficiently precise calculation of the *r*-values (ref. 12) and, unfortunately, most experimental data do not answer this requirement.

It may be concluded that the procedures quoted are suited neither to a precise determination of the monomer reactivity ratios nor to the investigation of the consistency of the experimental data with the proposed model. An improved experimental approach will be enunciated in chapter 4.

REFERENCES

1 F.R. Mayo and F.M. Lewis, *J. Am. Chem. Soc.*, 66 (1944) 1594.
2 M. Fineman and S.D. Ross, *J. Polymer Sci.*, 5 (1950) 259.
3 L.J. Young, *J. Polymer Sci.*, 54 (1961) 511.
4 T. Alfrey, J.J. Bohrer and H. Mark, *Copolymerization*, (1952) 12, Interscience Publishers, Inc., New York.
5 J. Schaefer, *J. Phys. Chem.*, 70 (1966) 1975.
6 T.K. Wu, *J. Phys. Chem.*, 73 (1969) 1801.
7 T.K. Wu, *J. Polymer Sci. A-2*, 8 (1970) 167.
8 D.W. Behnken, *J. Polymer Sci. A*, 2 (1964) 645.
9 P.W. Tidwell and G.A. Mortimer, *J. Polymer Sci. A*, 3 (1965) 369.
10 H. James Harwood, N.W. Johnston and H. Piotrowski, *J. Polymer Sci. C*, 25 (1968) 23.
11 R.K.S. Chan and V.E. Meyer, *J. Polymer Sci. C*, 25 (1968) 11.
12 D.R. Montgomery and C.E. Fry, *J. Polymer Sci. C*, 25 (1968) 59.

CHAPTER 4

A DETAILED DETERMINATION BY MEANS OF QUANTITATIVE GAS-LIQUID CHROMATOGRAPHY OF THE COURSE OF COPOLYMERIZATION REACTIONS

4.1 INTRODUCTION

In chapter 3 a summary has been given of the several known methods of determining *r*-values, and the common disadvantages of these methods have been discussed.

The main feature of the improved experimental method described in this chapter is that it eventually will afford (see chapter 5) the possibility of frequent determination of the numbers of moles (except for a constant) of both monomers during copolymerization experiments up to 20-40% conversion. Thus the method will offer the possibility of generating curves of monomer quantity versus reaction time or degree of conversion by non-linear least-squares methods (see chapter 7). This approach will lead to an extended accessibility of the characteristic variables, viz. the monomer feed composition and the degree of conversion. Consequently, this experimental method and the subsequent computational procedure to determine the *r*-values do not show any of the disadvantages of the usual methods cited in chapter 3.

The advantages of the present method include the omission of copolymer analysis with its accompanying errors. When gaseous monomers are involved the method is particularly favourable.

4.2 PRINCIPLES OF OPERATION

The reactor is a vertically placed cylindrical vessel provided with a piston. The upper compartment serves as reaction chamber, the lower compartment to control the pressure. The liquid monomer (vinylacetate) and the solvent (*tert*-butylalcohol (TBA)), containing the radical initiator (α,α'-azodiisobutyronitrile), are introduced into the reaction chamber. The approximate amount of the gaseous monomer (ethylene) required is dissolved in the liquid at 30 kgf/cm^2 and at 62°C (reaction temperature). The gas phase is vented at constant pressure. Next, in order to undersaturate the liquid phase with ethylene, this phase is pressurized up to 35 kgf/cm^2. Reaction starts approximately half an hour after reaching reaction conditions.

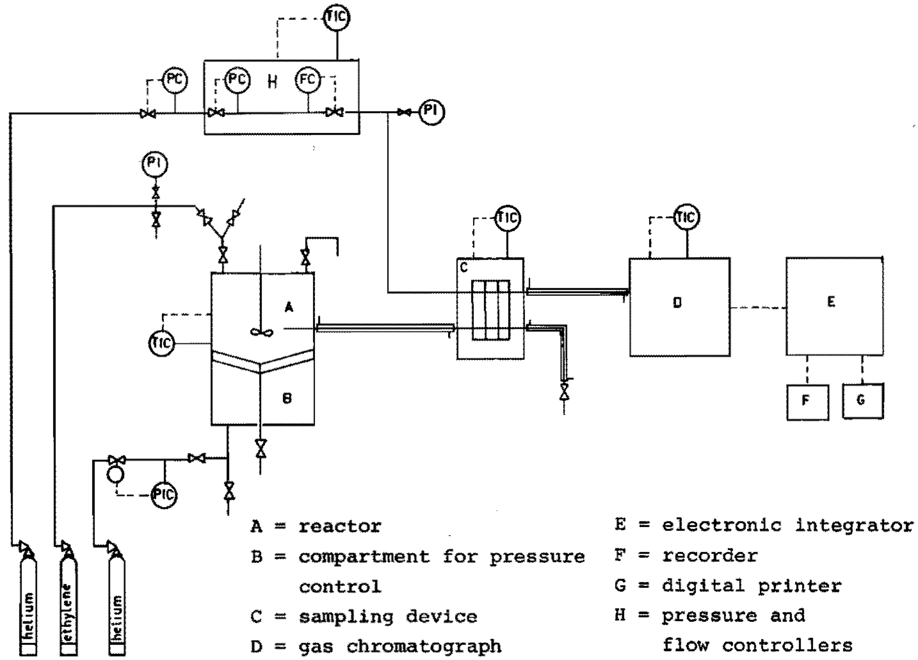
By means of a disc valve samples of constant volume are taken from the reactor every 10 minutes during 8-10 hours and introduced into a gas chromatograph. In the sampling system the sample remains at reaction conditions (35 kgf/cm^2 and 62°C) until the very moment of expansion and vaporization in the carrier gas stream of the gas chromatograph. Copolymer present in the sample is retained by a precolumn. The peak areas of the three remaining components (ethylene, vinylacetate and TBA) are determined by electronic integration of the detector signal and printed out by a digital printer.

The analytical system is calibrated by injecting, by means of the same sampling device, samples of the pure monomers ethylene and vinylacetate, which have well-known densities under the appropriate conditions.

From the changes in the peak area of the inert solvent, the contraction due to polymerization can be derived. The changes in monomer concentration, *merely* due to copolymerization can thus be determined from samplings by the constant-volume sampling device. In chapter 5 it will be shown in what way the numbers of moles ethylene and vinylacetate in the reactor can be derived (except for a constant) from the measured peak areas and the reference injection data, at any sampling moment, i.e. about every ten minutes.

4.3 APPARATUS

A block diagram of the system and its components is shown in Fig. 4-1.



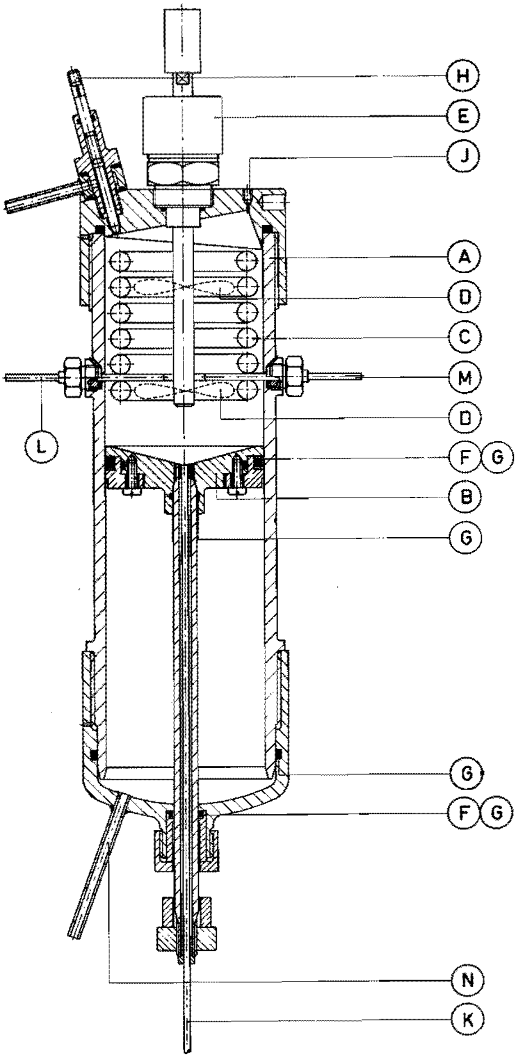
A = reactor
B = compartment for pressure control
C = sampling device
D = gas chromatograph
E = electronic integrator
F = recorder
G = digital printer
H = pressure and flow controllers

Fig. 4-1 Simplified scheme of the integral equipment

4.3.1 THE REACTOR

In earlier, explorative investigations (ref. 1) on ethylene-vinylacetate copolymerization, reactor types have been used which had the disadvantage of containing a liquid phase as well as a gas phase. This results in a continuous reestablishment of the equilibrium between the gas phase and the liquid reaction phase during reaction. Thus, changes in monomer concentrations in the liquid phase are no longer caused by reaction only, and this makes it complicated to follow the reaction in detail.

The reactor used in this research comes up to the requirement of a *closed* reaction system with *one* (liquid) phase. In order to attain one reaction phase a construction had to be applied rendering it possible to expell the gas phase completely after dissolving the required amount of ethylene in the liquid phase. This condition was met by a cylindrical vessel



A = reactor wall (AISI 316 stainless steel)
B = piston
C = heating coil
D = propeller type stirrer
E = stuffing box
F = Teflon cuff
G = Viton "O" ring
H = reactor inlet
J = vent
K = reactor drain
L = sampling tube
M = thermo-well
N = helium supply tube

Fig. 4-2 Constructional drawing of the reactor

provided with a piston, the piston shaft moving through a seal in the bottom of the vessel. The reactor is shown in Fig. 4-2.

The reaction takes place in the compartment above the piston. Below the piston helium can be introduced in order to pressurize the vessel. The reactor inlet (H in Fig. 4-2) is intended for the introduction of the liquid as well as the gaseous components. The reactor has three outlets:

(J in Fig. 4-2)	at the very top of the reaction compartment to expell the excess of gaseous components,
(K in Fig. 4-2)	in the centre of the piston, to drain the reactor through a capillary tube in the hollow piston rod, and
(L in Fig. 4-2)	in the middle of the reactor, to take samples from the reactor.

The top of the reactor has been bevelled intentionally to ensure complete escaping of the gas phase.

A special stuffing box (E in Fig. 4-2) was constructed, combined with axial and radial bearings, which ensures good stirring at 500-1500 r.p.m. under reaction conditions (62°C and 35 kgf/cm^2).

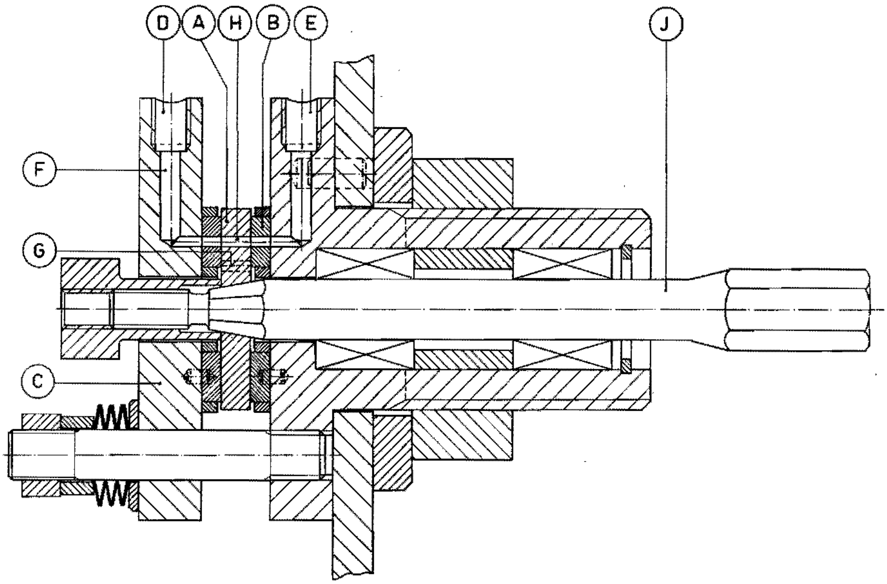
Stirring is accomplished by two three-blade stirrers of the propeller type, attached to one shaft at heights of approximately 1/3 and 2/3 of the reaction compartment.

The reactor is provided with an internal helical tube, through which water is circulated by a thermostat. The temperature of the thermostat is kept at 66°C. The reactor temperature is controlled at 62°C ± 0.2 by regulating the amount of circulating water.

The connection between the sample outlet (L in Fig. 4-2) and the sampling system is a capillary tube (0.5 mm i.d.), whose temperature (62°C) is controlled by a thermostat. Although not stirred, the capillary tube, being under the same conditions of temperature and pressure as the reaction vessel, simply forms an extension of the reactor.

4.3.2 THE SAMPLING SYSTEM

The first step in the analysis is sampling from the reactor, which is at a pressure of 35 kgf/cm^2. At this pressure level, a sampling repeatability range of 0.1% is required at a sample size of the order of magnitude of some microlitres.



A = steel disc
B = plastic sealing ring
C = valve body
D = sample inlet
E = sample outlet
F = sample canal
G = carrier gas canal
H = sample chamber
J = spindle

Fig. 4-3 The sampling valve

The principles of the sampling valve are shown in Fig. 4-3. The valve body contains two canals of 1.5 mm i.d.. One of these is incorporated in the carrier gas system of a gas chromatograph, the other is connected to the sample tube emerging from the reactor. The two plastic sealing rings (B in Fig. 4-3) are attached to the valve body by means of dowels. The steel disc (A in Fig. 4-3) can be turned between the two sealing rings by means of the shaft (J in Fig. 4-3). The steel disc is provided with six bores, one of them forming the sample volume. By turning the disc over 60° the volume of the bore is introduced into the carrier gas stream.

A requirement on the sampling valve is to be gas-tight at 40 kgf/cm^2. To ensure a reasonable operating torque at the necessary sealing pressure, the sealing materials to be applied must exhibit:

low static friction
low dynamic friction
low stress relaxation
high scratch resistance
good sealing properties

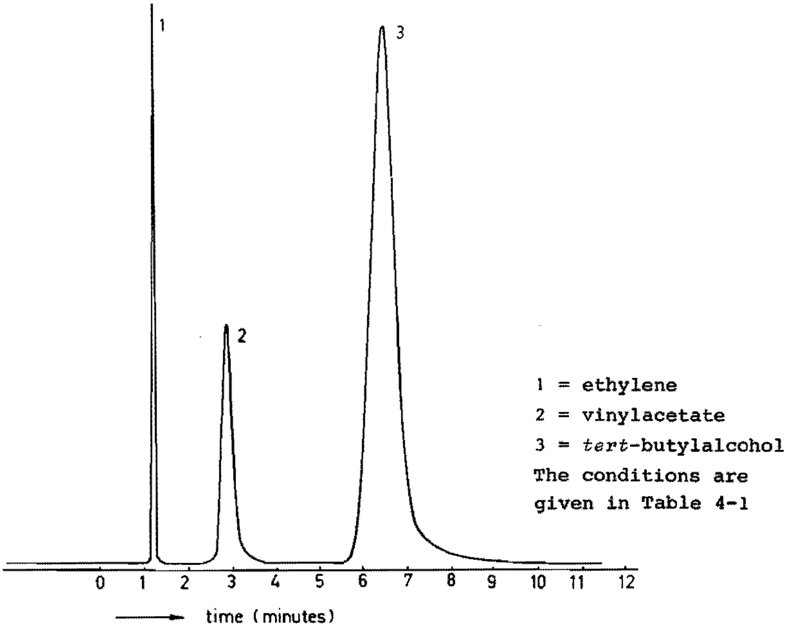
Sealing materials for these purposes have been developed during this research (ref. 2) based on Kel F - Teflon - Molykote blends and special sintering techniques.

It is essential that the sample in the sampling valve is under the conditions of temperature and pressure of the reactor. Any temperature or pressure difference may cause phase separation and thus decrease sampling accuracy. For these reasons the sampling valve is placed in an air bath kept at 62°C ± 0.05 . Moreover, restrictions between the reactor and the sampling valve are avoided and flushing of the sampling system takes place by means of a needle valve situated *behind* the sampling valve.

In the carrier gas stream between the sampling valve and the gas chromatograph a precolumn is placed, 3 cm long and ¼" in o.d., packed with glass fibre and controlled at 75°C ± 0.1 . The precolumn is used to retain the very small amounts of polymer from the injected samples and to vaporize the liquid components.

4.3.3 THE GAS CHROMATOGRAPH

The gas chromatograph used is a modified Hewlett-Packard (F & M Scientific Division) model 720, in which all control systems have been replaced by more accurate controllers to meet the accuracy claimed (see 4.4). High accuracy in temperature controlling is achieved, using proportional temperature controllers with adjustable integral and derivative action (Eurotherm type PID/SCR-10).



1 = ethylene
2 = vinylacetate
3 = *tert*-butylalcohol
The conditions are
given in Table 4-1

Fig. 4-4 Typical chromatogram

A typical chromatogram is shown in Fig. 4-4 and the experimental conditions of the gas chromatograph are listed in table 4-1.

4.3.4 ELECTRONIC INTEGRATORS

In order to determine the peak areas the detector output is connected to an electronic integrator (Infotronics type CRS-100 or CRS-110). It appeared that electronic integrators may exhibit considerable deviations from linearity. To regard the linearity of electronic integrators as a reliable feature merely because it cannot simply be verified, appears very dangerous. In behalf of the research described in this thesis a comparatively simple method has been developed to check the linearity of the integrators.

Table 4-1 Experimental conditions of the gas-chromatographic system

column	3-metre stainless steel coiled tubing ¼" o.d.
solid support	chromosorb G 60-80 mesh (acid washed and treated with dimethylchlorosilane) Hewlett-Packard
stationary phase	10% by weight of a mixture of diglycerol and carbowax 400 (60/40% by weight)
carrier gas	helium dried over Linde molecular sieves (type 5 A, 1/8" pellets)
flow control	accomplished by the combined action of the following devices connected in series in the order as indicated (all pressures are absolute): - reducing valve on cylinder, 200-5 kgf/cm^2; - reducing valve (Negretti) at room temperature, 5-4 kgf/cm^2; - reducing valve (Negretti) thermostatically controlled at 25°C ± 0.05, 4-3 kgf/cm^2; - flow controller (Brooks model 8743), thermostatically controlled at 25°C ± 0.05, flow rate 1 cm^3/sec, column inlet pressure 1.5 kgf/cm^2, column outlet pressure: atmospheric.
column temperature	75°C ± 0.05
detector	heat conductivity cell (Gow-Mac, semi-diffusion type) temperature 108°C ± 0.05
bridge current	150-200 mA, current stabilization by means of a d.c. power supply unit (Hewlett-Packard type 6112A)
injection mode	the sample is injected directly into the precolumn (described in 4.3.2), which also serves as vaporizing chamber. The precolumn as well as the tube (1/8" o.d.) connecting it with the gas-chromatographic column are kept at 75°C ± 0.1 .

4.4 ACCURACY OF ANALYSIS

4.4.1 REPEATABILITY

The peak area determined by integration of the detector signal is given by the following equation (ref. 3):

$$A = k \frac{S}{D} M \qquad (4\text{-}1)$$

with A = peak area
k = constant for gas chromatograph and integrator combination
S = detector sensitivity
D = mass flow rate of carrier gas
M = total mass of one component from the sample

The detector sensitivity S depends on the bridge current I (ref. 3):

$$\frac{dS}{S} = 3 \frac{dI}{I}$$

Table 4-2 lists the estimated contributions of the different factors to the measured peak area repeatability range.

Table 4-2 Survey of the various factors affecting the peak area repeatability range

factor	affected parameter in equation (4-1)	influence on peak area repeatability[1]	
		short-term changes < 2 hours	long-term changes 0 - 12 hours
sample size	M	0.1%	0.1%
column oven temperature	D	-	0.05%
carrier gas flow rate	D	-	0.05%
detector sensitivity	S	-	0.1%
integrator	k[2]	0.2%[2]	0.2%[2]
	k[3]	0.6%[3]	0.6%[3]
Total repeatability range for the determination of a peak area		0.3%[2] 0.7%[3]	0.5%[2] 0.9%[3]

1) A repeatability range of x% denotes that 90% of all observations lie between +½x% and -½x% from the mean value.

2) for ethylene and vinylacetate peaks

3) for TBA peaks

The possibility of carrying out gas chromatography with the precision claimed, under the relevant conditions, is confirmed by Goedert and Guiochon (ref. 3).

4.4.2 LINEARITY OF THE ANALYTICAL SYSTEM

As the composition of the monomer feed and the degree of conversion will be calculated by equations (5-11) and (5-13), the linearity of the integral analytical system has to be investigated. The results are given in Table 4-3.

Within one kinetic series the estimated mean value of the error due to non-linearity is 0.2% for the determination of ratios of peak areas from the same component.

Table 4-3 Factors affecting the linearity of the analytical system

factor	non-linearity 1)	region	remarks
pressure dependence of sample size	1.2%	1 - 35 kgf/cm^2	irrelevant if all samples are taken at the same pressure level (see 5.3.3)
integrator	0.25%	0.1 - 60 mV input signal	investigated by integration of block functions
detector	0.2%	quantities to be detected varying from 1.5 x 10^{-6} to 50 x 10^{-6} mol; peak crest concentrations varying from 0.5 - 5 mol % in the carrier gas	determined by injecting such amounts of ethylene and such compositions of vinylacetate/TBA mixtures as to cover the region mentioned
peak separation	0.1%	all experiments	complete baseline recovery between all peaks

1) Non-linearity x% means: the maximum deviation from linearity in the region indicated is +½x% or -½x%, the middle of the region having deviation zero by definition.

4.5 CONCLUSION

The gas-chromatographic method described in this chapter can basically provide sufficient information to characterize the course of a copolymerization reaction in detail. From the experimentally observable parameters (peak areas), the monomer quantities in the reactor will have to be calculated (see chapter 5). In order to estimate the error in the latter, the discussion of the repeatability of the measured peak areas and the linearity of the analytical system, as given in this chapter, is a necessity.

REFERENCES

1 L.C. Rouschop and H.P.H. Vrijens, *Internal Reports Eindhoven University of Technology*, Polymer Technology Section (1965).

2 J.A. Michiels and A.L. German, *Internal Report Eindhoven University of Technology*, Polymer Technology Section (1968).

3 M. Goedert and G. Guiochon, *Advances in chromatography*, Proceedings of the Fifth International Symposium, Las Vegas (1969), Preston Technical Abstracts Company Evanston, Illinois.

CHAPTER 5

DERIVATION OF THE RELATIONSHIP BETWEEN THE COMPOSITION OF THE REACTION MIXTURE AND THE PRIMARY EXPERIMENTAL DATA

In chapter 4 an experimental procedure has been described, based on quantitative gas chromatography. As a result of any one sampling from the reactor three peak areas arose, representing the concentrations of the two monomers and the solvent. In behalf of the computation of the monomer reactivity ratios, however, the monomer feed composition and the degree of conversion have to be calculated from the measured peak areas. The relations concerned will be derived in this chapter and the error in the resulting parameters will be estimated.

5.1 INTRODUCTION

The monomer feed composition and the corresponding degree of conversion are calculated from the measured peak areas with the aid of the peak areas from reference injections. Reference injections are samples of pure ethylene and pure vinylacetate, injected under the same conditions and with the same sampling valve as used for sampling from the reactor. The densities of the reference monomers under these conditions are well known either from tables for ethylene, or by own measurements for vinylacetate (see 5.3).

As stated before, the copolymerization equation has only general validity if *numbers of moles* are substituted. The reaction volume is not necessarily constant under this condition. However, since the sampling valve takes samples of a *constant volume* at any reaction time during a kinetic experiment, the contraction of the system due to copolymerization has to be taken into account.

5.2 DERIVATION OF THE MONOMER FEED COMPOSITION AND THE DEGREE OF CONVERSION FROM THE MEASURED PEAK AREAS

From chapter 7 it will become clear that an attractive method of calculating r-values requires the determination of $q = n_e/n_v$ at a series of degrees of conversion f_v, where:

- n_e = number of moles ethylene in the reactor,
- n_v = number of moles vinylacetate in the reactor, and
- f_v = the degree of conversion based on vinylacetate.

The symbols used in the derivation are:

c = molar concentration	e = ethylene
n = number of moles	v = vinylacetate
A = peak area	b = *tert*-butyl alcohol (TBA)
V = reactor volume	s = sample
f = degree of conversion	r = reference

The sampling valve introduces a *constant volume* into the gas chromatograph and for that reason *concentrations* are determined by:

$$c_{es} = \frac{A_{es}}{A_{er}} \times c_{er} \tag{5-1}$$

with c_{es} = concentration of ethylene in the sample = concentration of ethylene in the reactor
A_{es} = peak area of ethylene from a sample injection
A_{er} = peak area of ethylene from a reference injection
c_{er} = the ethylene concentration of the reference injection

Similarly:

$$c_{vs} = \frac{A_{vs}}{A_{vr}} \times c_{vr} \tag{5-2}$$

and

$$c_{bs} = \frac{A_{bs}}{A_{br}} \times c_{br} , \tag{5-3}$$

where $c_{br} = c_{bs}$ at $f_v = 0$ by definition.

However, n_e and n_v have to be determined:

$$n_e = c_{es} \times V(f_v) \tag{5-4}$$

with $V(f_v)$ = reactor volume at the degree of conversion f_v.
Consequently:

$$\frac{n_e}{V(0)} = c_{es} \times \frac{V(f_v)}{V(0)} \tag{5-5}$$

with $V(0)$ = reactor volume at zero conversion.
The solvent TBA is not consumed by reaction, i.e. n_b = constant, and consequently equation (5-3) leads to:

$$\frac{n_b}{V(f_v)} = \frac{A_{bs}}{A_{br}} \times \frac{n_b}{V(0)} , \tag{5-6}$$

which reduces to:

$$\frac{V(f_v)}{V(0)} = \frac{A_{br}}{A_{bs}} \tag{5-7}$$

Combination of equations (5-5) and (5-7) gives:

$$\frac{n_e}{V(0)} = c_{es} \times \frac{A_{br}}{A_{bs}} \tag{5-8}$$

and finally (5-1) and (5-8) yields:

$$\frac{n_e}{V(0)} = \frac{A_{es} \times A_{br}}{A_{er} \times A_{bs}} \times c_{er} \tag{5-9}$$

In the same way:

$$\frac{n_v}{V(0)} = \frac{A_{vs} \times A_{br}}{A_{vr} \times A_{bs}} \times c_{vr} \tag{5-10}$$

The quantities $n_e/V(0)$ and $n_v/V(0)$ have the dimension of concentration. They are, however, only real concentrations at zero conversion. Generally, these quantities are numbers of moles divided by the reaction volume at zero conversion.
From (5-9) and (5-10) follows:

$$q = \frac{n_e}{n_v} = \frac{A_{es} \times A_{vr} \times c_{er}}{A_{vs} \times A_{er} \times c_{vr}} \tag{5-11}$$

and

$$\frac{n_v}{(n_v)_o} = \frac{A_{vs} \times (A_{bs})_o}{A_{bs} \times (A_{vs})_o} \tag{5-12}$$

from which the conversion based on vinylacetate can be calculated as:

$$f_v = 100 \left\{ 1 - \frac{n_v}{(n_v)_o} \right\} \% , \tag{5-13}$$

where the subscript zero indicates the conditions at zero conversion.

The peak areas, either from sample or reference injections, are supplied by the gas-chromatographic measurements described in chapter 4. It becomes evident from equation (5-11) that the determination of $q = n_e/n_v$ necessitates the knowledge of the density of the ethylene and vinylacetate references under the relevant conditions.

5.3 THE ETHYLENE AND VINYLACETATE REFERENCES

5.3.1 CALCULATION OF THE DENSITY OF THE ETHYLENE REFERENCE

In behalf of the calculation of the density of the injected ethylene sample, the data from two publications are combined. On the one hand Walters et al. (ref. 1) give a series of "compressibilities" (z-values) for ethylene at pressures varying from 50 to 600 p.s.i.a. (3.5 to 42.2 kgf/cm^2) and temperatures between 20°F and 100°F (-7°C and 38°C). On the other hand, Michels and Geldermans (ref. 2) report a series of densities of ethylene, expressed as values of the *PV* product in dependence of *P* and *T*, at pressures varying from 16-400 kgf/cm^2 and temperatures between 0°C and 100°C with intervals of 25°C.

After combining the two data sources in question, the density of ethylene under "reference injection" conditions is determined by interpolation:

$$\begin{aligned}\rho_e &= 40.36 \text{ g/dm}^3 \text{ at } 62.0^\circ\text{C and } 35.04 \text{ kgf/cm}^2 \\ &= c_{er} = 1.439 \text{ mol/dm}^3\end{aligned}$$

5.3.2 MEASUREMENT OF THE DENSITY OF THE VINYLACETATE REFERENCE

Since the literature gives only little information of unknown reliability, investigation of the density of vinylacetate under reference conditions is necessary. The measurements have been carried out by means of a special pycnometer, designed for measurement at elevated temperatures.

Using $\rho_{H_2O}^{62} = 0.9822$ g/cm^3 from (ref. 3), it follows that

$$\begin{aligned}\rho_v^{62} &= 0.8802 \text{ g/cm}^3 \\ &= 0.8792 \text{ g/cm}^3 \text{ (duplicate determination)}\end{aligned}$$

The value used in all calculations is chosen as

$$\begin{aligned}\rho_v^{62} &= 879.7 \text{ g/dm}^3 \\ &= c_{vr} = 10.22 \text{ mol/dm}^3\end{aligned}$$

In addition, the reliability of this value is confirmed by calculating the density of vinylacetate with data from (ref. 4):

$$\rho_v^{62} = 879.6 \text{ g/dm}^3$$

5.3.3 PRESSURE DEPENDENCE OF THE SAMPLE VOLUME

It appears from equation (5-11) that the calculation of the molar feed ratio requires a constant sample size only during the *reference* injections. This constant sample size has been chosen equal to the volume of the sample chamber at 62°C and 35 kgf/cm^2. Since the ethylene reference injections are carried out at a pressure level of 35 kgf/cm^2, whereas the vinylacetate reference injections are performed at atmospheric pressure (see 6.2.3), it is necessary to determine the pressure dependence of the sample size.

The expansion of the sample volume was determined by performing a series of samplings from a liquid with known compressibility (viz. ethyl acetate) at increasing pressures up to 35 kgf/cm^2. The samples passed through the analytical system under exactly the same conditions (see 6.5.1) as did the reference injections and the samples from the reactor, and the corresponding peak areas were determined.

The mean value of the peak areas of ethyl acetate samples injected at 35 kgf/cm^2 minus the mean value of the peak areas of the samples injected at atmospheric pressure, was 1.5% of the latter value.

The compressibility of ethyl acetate was given by (ref. 5):

$$\beta = -\frac{1}{V_o}\left(\frac{\partial V}{\partial p}\right)_T = 103.10^{-6}\ \text{bar}^{-1} \text{ at 23 bar and } 13^\circ\text{C}$$

$$= 90.10^{-6}\ \text{bar}^{-1} \text{ at 200 bar and } 20^\circ\text{C}$$

At pressures up to 35 kgf/cm^2 and at 62°C $\beta \simeq 10^{-4}$ cm^2/kgf seemed a good estimation. The compression of ethyl acetate at 35 kgf/cm^2 could then be calculated as:
$100 \cdot \beta \cdot \Delta p = 100 \cdot 10^{-4} \cdot (35 - 1) \simeq 0.3\%$ of the volume at atmospheric pressure.

Conclusion: the sample size at 35 kgf/cm^2 is 1.5% - 0.3% = 1.2% larger than at atmospheric pressure. (Further support for this assignment is provided by experiments in which ethylene is injected at increasing pressures from atmospheric to 35 kgf/cm^2). Consequently, the measured peak areas of the vinylacetate reference injections have to be increased by 1.2% before they enter into the calculations. The vinylacetate reference peak areas A_{vr} mentioned in the present investigation have already been corrected.

5.4 AN ESTIMATION OF THE ERROR IN DETERMINING THE MONOMER FEED RATIO AND THE DEGREE OF CONVERSION

The molar feed ratio $q = n_e/n_v$ and the reduced number of moles vinylacetate $n_v/(n_v)_o$ can be calculated from the primary experimental data with the equations (5-11) and (5-12).

$$q = \frac{n_e}{n_v} = \frac{A_{es} \times A_{vr} \times c_{er}}{A_{vs} \times A_{er} \times c_{vr}} \qquad ((5\text{-}11))$$

$$\frac{n_v}{(n_v)_o} = \frac{A_{vs} \times (A_{bs})_o}{A_{bs} \times (A_{vs})_o} \qquad ((5\text{-}12))$$

Some important remarks about equations (5-11) and (5-12):

- As A_{es}/A_{vs} , A_{vs}/A_{bs} and $(A_{bs})_o/(A_{vs})_o$ are ratios of peak areas resulting from any one sampling, these quantities are nearly independent of the error sources listed in Table 4-2, except for the repeatability range of the integrator, which was 0.4% for the first and the second and 1.2% for the third ratio.
- The value of $n_v/(n_v)_o$ is independent of sample size; once the reference samples have been injected, $q = n_e/n_v$ becomes independent of sample size.
- The error in A_{er}/A_{vr} due to non-repeatability only depends on the peak area repeatability range on short term (see Table 4-2), if the reference injections are carried out within an interval of 1.5 hours.

  The value of A_{er}/A_{vr} appears to be constant ± 0.3% during the experimental period of approximately one year. Since the calculations of *all* experiments are performed with the average value of $A_{er}/A_{vr} = 0.08254$, this ratio does not contribute to the random error in $q = n_e/n_v$.

- Also the ratio c_{er}/c_{vr} = constant does not contribute to the random error in $q = n_e/n_v$.
- These considerations, together with the data from Table 4-3 lead to the conclusion that the estimated mean error in the determination of

$$q = \frac{n_e}{n_v} \quad \text{is} \pm 0.3\% \;,$$

and of

$$\frac{n_v}{(n_v)_o} \quad \text{is} \pm 1.0\% \;.$$

The degree of conversion f_v is related to $n_v/(n_v)_o$ according to:

$$f_v = 100\left\{1 - \frac{n_v}{(n_v)_o}\right\}\%$$

For an average conversion of 20%, this means that the estimated absolute error in the determination of f_v is ± 0.8% (conversion).

The error estimations will appear to be useful in order to check the adequacy of the Alfrey model in the description of ethylene-vinylacetate copolymerization (see 7.5) and to compute the error in the resulting r-values (see 7.4.2).

REFERENCES

1 R.J. Walters et al., *Chem. Eng. Progr.*, 50 (1954) 511.
2 A. Michels and M. Geldermans, *Physica*, IX (1942) 967.
3 R.C. Weast et al., *Handbook of Chemistry and Physics*, 46th edition (1965).
4 S.A. Miller, *Acetylene, its properties, manufacture and uses*, vol. 2 (1966) 261, Ernest Benn Ltd., London.
5 J.H. Perry, ed., *Chemical Engineers' Handbook*, 4th edition (1963) 3-106, McGraw-Hill, New York.

CHAPTER 6

THE PERFORMANCE OF KINETIC EXPERIMENTS WITH THE SYSTEM ETHYLENE-VINYLACETATE

6.1 INTRODUCTION

The experimental method, providing the desired parameters after some transformations (see chapter 5), has been described in chapter 4. In the present chapter the performance of kinetic copolymerization experiments with the system ethylene-vinylacetate will be given in detail.

In the performance of the experiments several stages can be distinguished:

- the purification of the chemical compounds involved;
- filling the reactor with the required amounts of monomer, solvent and initiator, and subsequent pressurizing and heating up of the reaction mixture;
- the performance of reference injections with vinylacetate and ethylene;
- sampling from the reactor;
- termination of the process;
- determination of molecular weight and solution viscosity of the copolymers.

In addition, a survey will be given of the region of monomer concentrations covered by the kinetic experiments, and the phase behaviour of the reaction mixture in this region will be examined.

The results will be presented in such a form that they can be entered into the procedures for calculating the *r*-values (see chapter 7).

6.2 EXPERIMENTAL PROCEDURE

6.2.1 PURIFICATION OF THE CHEMICAL COMPOUNDS

Ethylene

The ethylene used, supplied by the "Dutch State Mines", was of polymerization quality, containing as contaminations:

oxygen	<	10 ppm
water	<	10 ppm
carbon monoxide	<	10 ppm
acetylene	<	5 ppm
acetone	<	5 ppm

The ethylene was used in the copolymerization experiments without further purification.

Vinylacetate

The vinylacetate (Konam), containing hydroquinone (inhibitor), water, acetic acid, acetaldehyde and polyvinylacetate as main impurities, had to be purified by distillation prior to copolymerization. The fractionation was carried out in a column (height 1.60 m, diameter 36 mm) packed with glass Fenske helices of 3 mm diameter. This column was capable of separating the azeotrope water-vinylacetate (b.p. 66°C and containing 7.3% by weight water (ref. 1)) from pure vinylacetate (b.p. 72.7°C) at a capacity of 500 cm^3 distillate per hour and a reflux ratio of 5. The fraction with a boiling range of 72-73°C was collected. This fraction had a refractive index $n_D^{20} = 1.3955 - 1.3956$, whereas in (ref. 2) a refractive index $n_D^{20} = 1.3956$ was reported for pure vinylacetate. By gas-chromatographic analysis, the remaining impurity content (predominantly water and acetaldehyde) was estimated to be approximately 0.1% .

tert-Butyl alcohol (TBA)

The solvent TBA (Shell) was purified by distillation in a similar column as described for the distillation of vinylacetate at a capacity of 250 cm^3 distillate per hour and a reflux ratio of 10. The fraction with a boiling range of 82-83°C and a refractive index n_D^{27} = 1.3842 - 1.3844 was collected. According to (ref. 3) the boiling point of pure TBA was 82.6°C and the refractive index n_D^{27} = 1.3843 . The remaining impurity content (predominantly water) was estimated to be 0.1% by means of gaschromatographic analysis.

6.2.2 INTRODUCTION OF THE COMPONENTS INTO THE REACTOR

Before turning to the filling procedure, the reactor was rinsed with a mixture of *tert*-butyl alcohol and vinylacetate. The initiator (α,α'-azodiisobutyronitrile) was dissolved in the main part of the required mixture of vinylacetate and *tert*-butyl alcohol, and introduced into the reactor. Afterwards the remaining part of the mixture (without initiator) was added, by which the filling device was cleared from initiator.

After the liquid components were introduced, the reactor was allowed to reach reaction temperature (62°C). During the warming-up period, the reactor was flushed with ethylene in order to remove any penetrated air. This was achieved by admitting an ethylene pressure of about 10 kgf/cm^2 over the liquid, stirred slowly at 50 r.p.m.. Subsequently, the vessel was depressurized slowly. This procedure was repeated three times.

As soon as the reaction temperature was reached the approximate amount of ethylene required was dissolved in the liquid at a stirring speed of 500 r.p.m. and an ethylene pressure of 30 kgf/cm^2. The required amount of ethylene was empirically related to the dissolving time, varying from 1 to 30 minutes. Care was taken that the liquid surface during dissolving was not at such a level as to obstruct the reactor inlet; on the other hand, the piston should not be at its lowest position. In order to prevent large forces to be exerted on the reactor casing by the piston, the latter must stay floating, necessitating simultaneous control of the ethylene pressure on top of the piston and the helium pressure underneath.

At the expiry of the estimated dissolving time the stirring was temporarily stopped, the reactor inlet was shut off and the gas phase in the reactor was vented by means of a needle valve on the very top of the reactor. During this procedure the pressure in the reaction chamber was kept at 30 kgf/cm^2 by controlling the helium pressure under the piston.

After the gas phase had been completely removed from the reactor, which could be recognized by liquid delivery from the venting valve, pressure was increased up to the working pressure of 35 kgf/cm^2. This precaution was taken in order to prevent the development of a gaseous phase in the reactor. Such a situation might occur if:

<u>a</u> the temperature exceeded the saturation temperature;
<u>b</u> the pressure dropped below saturation pressure;
<u>c</u> the solubility of ethylene in the liquid mixture was diminished by polymer formation.

When the working pressure (35 kgf/cm^2) was chosen approximately 5 kgf/cm^2 above the maximum saturation pressure (30 kgf/cm^2), the liquid became undersaturated. Under the experimental conditions described later on (see 6.5) no indications were found for the existence of a gaseous phase during copolymerization.

The working pressure had to remain essentially constant during a copolymerization experiment and was controlled by an electronic system, with an accuracy of ± 0.02 kgf/cm^2. The absolute pressure level was less important and was reproduced from one experiment to another with an accuracy of 35.0 kgf/cm^2 ± 0.1 .

A short time after completion of the filling procedure the reactor temperature was stabilized at 62°C ± 0.2 . Owing to an induction period, common in radical polymerization, the reaction started about half an hour after this moment, as could be seen from the gas-chromatographic measurements.

6.2.3 INJECTION OF THE REFERENCE MONOMERS

As already pointed out in chapter 5 both types of reference injections essentially have to be performed within as short a time interval as possible.

Ethylene reference injections

The pure ethylene supply tube was connected to the sample inlet of the sampling system and the sample valve was flushed. In the supply tube a provision was made to insert a high precision pressure gauge (± 0.01 kgf/cm^2), on which to read the ethylene pressure. The ethylene reference injections were carried out at 35 kgf/cm^2. About 5-10 reference samples were injected, thus providing a reliable average value for the reference peak area.

Vinylacetate reference injections

Vinylacetate was supplied to the sampling system by means of a syringe attached to the sample inlet connection of the sampling valve. After flushing the sampling system with vinylacetate at a slight pressure exerted by the syringe, the sample was allowed to warm up for two minutes and subsequently injected. In this way 5-10 vinylacetate reference peak areas were recorded, providing a reliable average value.

6.2.4 SAMPLING FROM THE REACTOR

After the reference peak areas were recorded, the sampling tube of the reactor was connected to the sample inlet of the sampling system and about every ten minutes a sample was injected. Preferably, the timing of the several experimental operations was such as to start the sampling from the reactor immediately after the reactor had reached reaction conditions. Prior to any injection to be carried out, the sampling tube was flushed by an amount of reaction mixture (approximately 2 cm^3), being slightly larger than the volume of this tube (1.5 cm^3).

Slightly dependent on the composition of the reaction mixture, the reaction started after about 3 sample injections (approx. ½ hour), which manifested itself from a distinct decrease of the ethylene and vinylacetate peak areas.

6.2.5 TERMINATION OF THE PROCESS

In dependence on the initial composition, a conversion of 20-40% (referring to vinylacetate) was reached within 4-6 hours. The reactor was drained and the reaction mixture was collected in a round-bottomed flask, containing ice and a small quantity of the inhibitor hydroquinone to stop the reaction. The copolymer was separated by steam distillation.

6.2.6 DETERMINATION OF MOLECULAR WEIGHT AND SOLUTION VISCOSITY

Each kinetic series yields a copolymer product with known mean composition. For each product the molecular weight has been determined by osmotic pressure measurements and the limiting viscosity number by measurement of the dilute solution viscosity.

The osmotic molecular weights were determined by means of a "High Speed Membrane Osmometer" (Hewlett-Packard model 502). Four solutions (of each sample) were prepared in toluene, containing 2 to 8 g copolymer per dm^3. The osmotic pressure π of the solutions was measured at 37°C. The values of $\frac{\pi}{c}$ (c = copolymer concentration in g/dm^3) were calculated and plotted against c. Using the linear least-squares method, straight lines were drawn through these points. The intercept on the $\frac{\pi}{c}$ axis provided the value at infinite dilution, $\left(\frac{\pi}{c}\right)_{c\to o}$. The mean osmotic molecular weight was then calculated according to Van 't Hoff's equation:

$$\overline{M}_{os} = \frac{RT}{(\pi/c)_{c\to o}}$$

In Table 6-1 the results are listed in the order of the products with increasing ethylene content. In addition, the mean value of the degree of polymerization ($\overline{D.P.}$) is calculated from $\overline{M}_{os}$ and the mean molecular weight of a monomer unit in the copolymer. The assumption here is that the osmotic molecular weight is not significantly larger than the number-average mo-

Table 6-1 Osmotic molecular weights and limiting viscosity numbers of the copolymer products

experimental code	initiator concentration mmol/dm^3	mol % ethylene in copolymer	$(\pi/c)_{c\to 0}$	$\overline{M}_{os}$	$\overline{D.P.}$	$[\eta]$ 100 cm^3/g
L	1.6	19.3	0.46	65300	872	0.43
B	2.4	21.2	0.55	55300	749	0.40
F	1.6	24.3	0.50	61000	847	0.42
E	1.6	28.9	0.56	54300	784	0.42
D	1.6	39.2	0.80	38000	600	0.43
J	2.8	40.0	0.99	30700	488	0.42
H	4.1	55.6	1.33	22800	424	0.40
A	3.3	60.0	1.35	22400	438	0.42
C	2.0	67.5	1.10	27600	588	0.45

lecular weight. In terms of qualitative judgement this supposition seems permissible, since equilibrium in the osmotic pressure measurements is reached comparatively soon, indicating a moderate contribution of low molecular weight species.

The viscosities of the dilute copolymer solutions in toluene were determined at 25°C in a "Ubbelohde" capillary viscometer placed in an automatic viscometer assembly (Hewlett-Packard model 5901 B). Of four solutions (of each sample) containing 0.1 to 0.5 g copolymer per 100 cm^3, the specific viscosity was determined from

$$\eta_{sp} = \frac{t - t_o}{t_o} ,$$

where t = the efflux time of the copolymer solution

and t_o = the efflux time of the pure solvent

The values of η_{sp}/c were plotted against c (c = the copolymer concentration in g/100 cm^3). Extrapolation to zero concentration yielded the limiting viscosity number $[\eta]$:

$$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c\to 0}$$

The results of the measurements of the limiting viscosity number are given in Table 6-1, listed in the order of the copolymer products with increasing ethylene content.

6.3 DESCRIPTION OF THE REGION OF MONOMER AND COPOLYMER CONCENTRATIONS COVERED BY THE KINETIC EXPERIMENTS

In Table 6-2 the kinetic experiments are listed, mentioning for each the initial monomer feed concentrations $(n_e/V(0))_1$ and $(n_v/V(0))_1$, the monomer feed "concentrations" at the end of the reaction $(n_e/V(0))_{end}$ and $(n_v/V(0))_{end}$, and the molar feed ratios $q_1 = (n_e/n_v)_1$ and $q_{end} = (n_e/n_v)_{end}$. In addition, the final copolymer concentrations are given.

Table 6-2 Survey of the region of monomer and copolymer concentrations covered by the kinetic experiments

experimental code	$\left(\frac{n_e}{V(0)}\right)_1$ mol/dm^3	$\left(\frac{n_v}{V(0)}\right)_1$ mol/dm^3	$\left(\frac{n_e}{V(0)}\right)_{end}$ mol/dm^3	$\left(\frac{n_v}{V(0)}\right)_{end}$ mol/dm^3	$q_1=\left(\frac{n_e}{n_v}\right)_1$	$q_{end}=\left(\frac{n_e}{n_v}\right)_{end}$	final copolymer concentration g/dm^3
A	1.81	0.90	1.40	0.63	2.00	2.22	34.7
B	0.44	1.22	0.28	0.64	0.36	0.45	54.5
C	2.08	0.76	1.79	0.62	2.74	2.88	20.1
D	1.08	1.21	0.82	0.82	0.89	1.00	40.9
E	0.89	1.63	0.63	0.99	0.55	0.64	62.3
F	0.52	1.15	0.41	0.83	0.45	0.50	30.6
H	1.26	0.73	1.06	0.57	1.72	1.86	19.4
J	1.22	1.33	0.88	0.82	0.92	1.07	53.5
L	0.43	1.32	0.29	0.76	0.32	0.39	52.0

In Fig. 6-1 a graphic representation is given of the ranges of both monomer "concentrations" for all experiments. The circles indicate the initial conditions, the dots those at the end of the reaction. The connecting lines do not pretend to describe the intermediate conditions and are drawn for ease of survey only. Each straight line drawn through the origin represents all combinations leading to a distinct molar feed ratio.

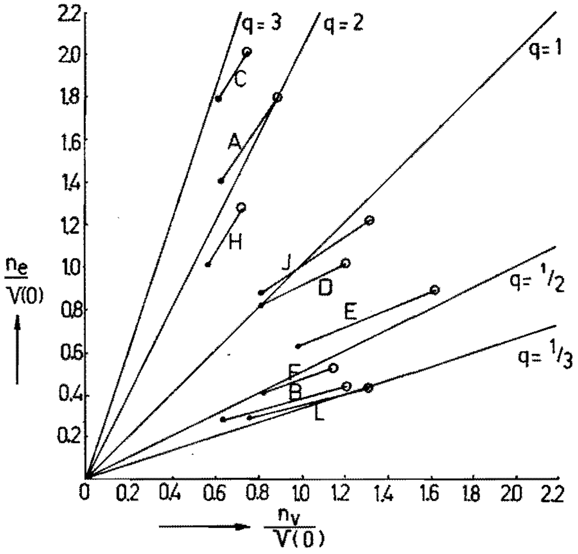


Fig. 6-1 Graphical survey of the monomer concentration range covered by the kinetic experiments

From the preceding data it can be concluded that the total monomer concentration range covered by all experiments lies between 0.91 and 2.85 mol/dm^3, while the molar ratio n_e/n_v varies between 0.32 and 2.88 (which means the mole fraction ethylene between 0.24 and 0.74).

6.4 EXAMINATION OF THE PHASE BEHAVIOUR

As already pointed out in 2.6, a condition for the application of the usual model for the description of copolymerization kinetics is the presence of only one liquid reaction phase. Thus, using the model, the phase behaviour should be examined.

For this purpose a number of representative experiments were carried out in a cylindrical glass vessel (capacity 500 cm^3, wall thickness 8 mm) under reaction conditions (viz. 35 kgf/cm^2 and 62°C). The vessel was frequently annealed and several other precautions were taken to protect the surroundings from the effect of possible explosion.

A number of experiments were conducted, covering the range of total molar concentrations and molar feed ratios (see 6.3) of the kinetic series from which the r-values had to be computed. The reaction mixtures were stirred at 100 r.p.m. and from time to time the stirring was stopped in order to examine the tendency towards phase separations in the reaction phase. The gas-chromatographic method described in chapter 4 was used to determine the initial molar feed ratio and the conversion. These experiments were, however, not suitable for evaluation of r-values since the existence of a small gas phase (see 4.3.1) could not be avoided in this type of reactor.

The results of the phase examination are given in Table 6-3.

It may be concluded from the data obtained in these experiments that the constraint of one liquid reaction phase is satisfied in the relevant region of monomer and copolymer concentrations. The slight turbidity shown by the reaction mixtures

Table 6-3 Results of the phase examination

phase experiment number	initial molar feed ratio q_o	total initial molar concentration mol/dm^3	conversion f_v in %	phase separation	remarks
1	0.30	1.56	44	none	clear solution
2	0.65	2.63	32	none	
3	0.98	2.75	30	none	
4	1.25	1.52	42	none	
5	1.97	2.07	33	none	
6	2.43	2.87	25	none	slight turbidity
7	2.85	1.26	39	none	
8	2.80	3.08	20	none	

yielding copolymers with high ethylene content, indicates, however, that precipitation might occur at still higher ethylene content in the copolymer.

6.5 PRESENTATION OF THE EXPERIMENTAL DATA AND PRELIMINARY TRANSFORMATIONS

6.5.1 SURVEY OF THE FIXED PROCESS AND ANALYSIS CONDITIONS

The process and analysis conditions, kept constant throughout the performance of all kinetic experiments, are listed in Table 6-4.

Table 6-4 Fixed process and analysis conditions

Total amount of liquid components (vinylacetate and *tert*-butylalcohol)	**750 cm^3**
Dissolving pressure for ethylene	**30 kgf/cm^2**
Working pressure	**35 kgf/cm^2**
Ethylene concentration of reference injection	**1.439 mol/dm^3**
Vinylacetate concentration of reference injection	**10.22 mol/dm^3**
Reaction temperature	**62°C**
Sampling valve temperature	**62°C**
Precolumn temperature	**75°C**
Column oven temperature	**75°C**
Detector temperature	**108°C**
Carrier gas flow rate	**1 cm^3/sec**
Bridge current	**150 mA**
Integrator baseline tracking up	**6 µV/min**
Integrator baseline tracking down	**60 µV/min**
Slope sensitivity	**0.3 µV/sec**
Input noise rejection	**position "3"**
Count rate	1000 counts/mV sec

6.5.2 SURVEY OF THE VARIABLE PROCESS CONDITIONS

The specific conditions for each kinetic experiment are the absolute amount of vinylacetate in the reactor, the dissolving time of ethylene and the amount of initiator added. These conditions are given in Table 6-5.

Table 6-5 Specific process conditions

experimental code	amount of vinylacetate in cm^3	dissolving time ethylene in min	amount of initiator in g
A	52	20	0.4
B	75	5	0.3
C	50	30	0.25
D	75	3	0.2
E	100	2	0.2
F	100	5	0.2
H	60	30	0.5
J	100	10	0.35
L	100	1	0.2

6.5.3 DATA FROM THE KINETIC 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 F are given as an example in Table 6-6.

The time basis and the values of A_{es}, A_{vs} and A_{bs} are provided by the digital printer during each kinetic series. From these values the molar feed ratio $q = n_e/n_v$ is calculated by equation (5-11):

$$q = \frac{n_e}{n_v} = \frac{A_{es} \times A_{vr} \times c_{er}}{A_{vs} \times A_{er} \times c_{vr}}$$

and finally the conversion based on vinylacetate is found by combining the equations (5-12) and (5-13):

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

Table 6-6 Measurements derived from kinetic experiment F, and basic transformations

Peak area of ethylene reference injection = A_{er} = 71042 counts
Peak area of vinylacetate reference injection = A_{vr} = 860698 counts

time min	A_{es} counts	A_{vs} counts	A_{bs} counts	$q = n_e/n_v$	f_v %
0.0	25535	97178	680725	0.4481	0.00
11.1	25376	96403	680715	0.4489	0.80
22.2	25187	95368	680755	0.4504	1.87
33.4	24910	93809	680654	0.4529	3.46
44.4	24565	92082	680739	0.4550	5.25
55.6	24189	90013	680828	0.4583	7.39
66.9	23919	88523	680109	0.4608	8.82
78.5	23588	86662	680491	0.4642	10.79
90.9	23285	85000	681589	0.4672	12.64
102.5	23000	83415	681942	0.4703	14.32
114.1	22706	81872	681056	0.4730	15.79
125.7	22503	80745	682106	0.4753	17.08
137.5	22148	79095	682697	0.4776	18.84
149.0	21859	77611	682283	0.4804	20.32
160.4	21630	76145	681628	0.4845	21.75
171.7	21354	74990	682257	0.4857	23.01
183.0	21153	73777	680550	0.4890	24.06
194.4	20884	72441	679953	0.4917	25.37
205.7	20647	70950	680949	0.4963	27.01
217.2	20461	70158	681109	0.4974	27.85

In this manner, each of the nine kinetic series produces a relatively large number (20-34) of experimental data pairs $(q_i, (f_v)_i)$, characterizing the course of the copolymerization reaction. In order to determine the monomer reactivity ratios, the experimental data pairs will be entered into the computational procedures described in chapter 7.

REFERENCES

1 S.A. Miller, *Acetylene, its properties, manufacture and uses*, vol. 2 (1966) 261, Ernest Benn Ltd., London.

2 R.A. Terteryan, A.I. Dintses and M.V. Rysakov, *Neftekhimiya*, 3 (1963) 719.

3 Landolt-Börnstein, *Zahlenwerte und Funktionen*, II. Band (1963) Springer-Verlag, Berlin.

CHAPTER 7

THE EVALUATION OF THE RESULTS

7.1 INTRODUCTION

Instead of one hardly accessible experimental data pair obtained by the classical experimental procedures in behalf of the determination of r-values (see chapter 3), the experimental method described in this thesis (see chapters 4 and 5) affords approximately 25 experimental data pairs per copolymerization experiment. This is accomplished by frequent measurement of the monomer feed composition during high-conversion copolymerization experiments with ethylene and vinylacetate (see chapter 6).

The substantially increased number of experimental data per kinetic series allows, as compared with other methods, a more precise evaluation of the monomer reactivity ratios. The computational procedure applied in this chapter guarantees efficient use of the extended amount of information and will be referred to as the "Feed Compositional Analysis (F.C.A.) method".

7.2 THE PRINCIPLES OF THE EVALUATION OF THE r-VALUES

For a certain conversion interval $0 - f_v$ the integrated form of the copolymerization equation (2-18) is given by:

$$f_v - 100\left\{1 - \left(\frac{q}{q_o}\right)^{-x_2-1}\left(\frac{x_2q - x_1}{x_2q_o - x_1}\right)^{x_1+x_2+1}\right\} = 0$$

with $x_1 = 1/(r_e - 1)$ and $x_2 = 1/(r_v - 1)$. The symbols have been explained in 2.3. Henceforth, precautions will be taken to avoid infeasible solutions of this equation by requiring $r_e \neq 1$ and $r_v \neq 1$ during all calculations concerned. In addition, the possible r-values will be confined to the significant, i.e. positive, values. The given model description can be formulated briefly as:

$$F\ (r_e,\ r_v,\ q_o,\ q,\ f_v)\ =\ 0$$

In chapter 6 it was shown that in this investigation the experimental data, after preliminary calculations, are available as a series of values $q_i = (n_e/n_v)_i$, describing the monomer feed composition at corresponding degrees of conversion $(f_v)_i$ for any kinetic experiment. Thus each kinetic series, producing g data pairs $(q_i,\ (f_v)_i)$, yields g conversion intervals $0 - (f_v)_i$ and consequently g equations F_i:

$$F_i\ =\ F\ (r_e,\ r_v,\ q_o,\ q_i,\ (f_v)_i)$$

with i = $1,\ldots.,g$
g = the number of data pairs resulting from one experiment

F_i represents the difference between the measured degree of conversion $(f_v)_i$ and the corresponding calculated expression for the degree of conversion, the latter being still an implicit function of r_e, r_v and q_o. The unknown parameters r_e and r_v are characteristic of the model, i.e. they are constants for all experiments, if the model is adequate. Parameter q_o is also unknown, but is characteristic of one distinct experiment. It represents the intercept on the q axis of a q versus f_v relation for any experiment. Consequently q_o will generally not be much different from q_1, which is the first measured value of q at zero conversion.

Owing to the experimental error, generally $F_i \neq 0$ $(i = 1,\ldots.,g)$ for any r_e, r_v and q_o combination.

The number of input data pairs per experiment (g) is of the order of magnitude of 25. So, theoretically, one single kinetic series gives sufficient information to determine the least-squares estimates for r_e, r_v and q_o by selecting those values of r_e, r_v and q_o that minimize:

$$\sum_{i=1}^{g} F_i^2 \ (r_e,\ r_v,\ q_o,\ q_i,\ (f_v)_i) \qquad (7\text{-}1)$$

leading to:

$$P = P\ (\hat{r}_e,\hat{r}_v,\hat{q}_o) = \sum_{i=1}^{g} F_i^2\ (\hat{r}_e,\hat{r}_v,\hat{q}_o,q_i,(f_v)_i) \qquad (7\text{-}2)$$

P = the residual sum of the squares of the deviations in f_v;
$\hat{r}_e$, $\hat{r}_v$ and $\hat{q}_o$ are the estimators of r_e, r_v and q_o, i.e. those parameters that minimize $\sum_{i=1}^{g} F_i^2$.

The implications of this approach will be discussed in 7.3, where the results of a necessarily adapted procedure (the F.C.A. method, procedure A) is given.

On the other hand, the information resulting from all kinetic experiments ($k = 1,\ldots.,n$) may be combined to determine the least-squares estimates for r_e, r_v and q_{ok}. This is achieved by selecting those values of r_e, r_v and q_{ok} that minimize:

$$\sum_{k=1}^{n} \sum_{i=1}^{g_k} F_{ik}^2\ (r_e,r_v,q_{ok},q_{ik},(f_v)_{ik}) \qquad (7\text{-}3)$$

leading to:

$$P = \sum_{k=1}^{n} P_k\ (\hat{r}_e,\hat{r}_v,\hat{q}_{ok})$$

$$= \sum_{k=1}^{n} \sum_{i=1}^{g_k} F_{ik}^2\ (\hat{r}_e,\hat{r}_v,\hat{q}_{ok},q_{ik}(f_v)_{ik}) \qquad (7\text{-}4)$$

with $i = 1,\ldots.,g_k$; g_k = number of input data pairs resulting from the kth experiment
$k = 1,\ldots.,n$; n = number of kinetic series

The results of this procedure (the F.C.A. method, procedure B) will be given in 7.4.

For the solution of the non-linear least-squares method, a computer program in Algol 60 is available (ref. 1). This program has been derived from a general procedure, reported by Lootsma (ref. 2), for solving constrained or unconstrained minimization problems.

Some remarks about the proposed estimation procedure

It can be seen that, even in the case of non-linear regression, the least-squares estimators of the parameters are identical with the maximum likelihood estimators, and therefore have desirable properties (ref. 3). However, some conditions must be met.

Primarily, the model must be consistent with the experimental data. It will be proved in 7.5 that this condition is satisfied.

Secondly, the random error in the indirectly observable response variables f_v and q should be independently and approximately normally distributed with a constant variance. Since the parameters f_v and q are calculated (see 5.2) from a number of experimentally observed variables (peak areas with most probably normal error distribution), the variance of f_v and q depends on f_v and q. But the variances of f_v and q change less than a factor 2, and it is believed from experience with related systems (ref. 4) that these small departures from normality and from a constant variance will not noticeably influence the results.

Another question of equal importance is inherent to the choice of minimizing the sum of the squares of the deviations in f_v. Here, for simplicity, the assumption has been made that only the observable response variable f_v contains an experimental error, whereas the errors in setting or determining the independent variable (i.e. $q = n_e/n_v$) are either zero or negligible. Though this condition is not met (see 5.4), there are no reasons for assuming that this might affect the results in the significant decimals, the more so as simulative computations, in which a suitable, normal error distribution is added to the functional values of q, do not reveal any significant discrepancy.

7.3 THE F.C.A. METHOD, PROCEDURE A

7.3.1 DISCUSSION OF THE PROCEDURE

As stated in the preceding section, one kinetic series might, in the absence of an experimental error, give sufficient information to determine the r-values by minimizing equation (7-1). Earlier, explorative investigations (ref. 5) have shown, however, that from the data of one single kinetic experiment no estimates $\hat{r}_e$ and $\hat{r}_v$ can be found for r_e and r_v, as the minimum of the function $\sum_{i=1}^{g} F_i^2 = P\ (r_e,\ r_v,\ q_o)$ is indeterminate. Instead of a single *point* in the r_e- r_v- q_o space, a *line* is found which virtually comes up to the constraint of $\sum_{i=1}^{g} F_i^2$ being minimal.

Any kinetic series affords such a line, which is approximately parallel to the r_e- r_v plane at various q_o levels. Supposing the model fits perfectly and no experimental errors are made, all experiments may be described with the aid of only one pair of r_e- r_v values (and as many q_o values as there are experiments). In this train of thought, each intersection point of the projections of the line minima on the r_e- r_v plane will yield an estimate for r_e and r_v. The precision of these estimates is determined by the angle between the intersecting lines; the slopes of these lines (which latter will appear to be practically straight) in the r_e- r_v plane depend on the average q values during the corresponding experiments. Thus, an area of more or less significant intersection points arises, from which for instance the centre of gravity is taken as the best estimate for r_e and r_v.

Some remarks in connection with the suggested procedure:

- The correlation between $\hat{r}_e$ and $\hat{r}_v$, as found from the information 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 small extent (average value 4.7% when compared with the region of

q values covered by all experiments (see 6.3)).

- An extreme example of this behaviour is seen by applying the differential form (i.e. an infinitesimal change of q) of the copolymerization equation to the data from a low-conversion experiment (see 3.1). Since in that case a linear relation between $\hat{r}_e$ and $\hat{r}_v$ is generated, $\hat{r}_e$ and $\hat{r}_v$ are 100% correlated.
- It is still useful to resort to the integral version of the copolymerization equation applied to a large number of experimental data per high-conversion experiment, instead of to the differential version, applied to two experimental data (mostly the initial feed composition and the mean copolymer composition) per low-conversion experiment. In the former case the line minimum contains the information supplied by a large number (approx. 25) of experimental data per experiment. Consequently, though $\hat{r}_e$ and $\hat{r}_v$ are highly correlated, a more accurate relation between $\hat{r}_e$ and $\hat{r}_v$ is provided than by the differential form.

7.3.2 ESTIMATION OF THE r-VALUES

On the ground of explorative investigations (ref. 5), the region where the more accurate r_e-value is to be expected can safely be chosen as $0.60 \leqslant r_e \leqslant 0.85$. In order to determine the relations between $\hat{r}_e$ and $\hat{r}_v$ mentioned, the experimental data $(q_i, (f_v)_i)$ of one kinetic experiment are substituted in equation (7-1). Thereupon r_e is successively assigned the values 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, and

$$\sum_{i=1}^{g} F_i^2 \; (r_e, r_v, q_o, q_i, (f_v)_i)$$

is minimized with respect to r_v and q_o. Each value of r_e provides estimates for r_v and q_o and a value of P = the residual sum of squares. Thus a relation between $\hat{r}_e$ and $\hat{r}_v$ is determined for the kinetic experiment in question.

This procedure is repeated for all kinetic series. The results are tabulated in Table 7-1.

Table 7-1 F.C.A.-A method; the computed values of r_v, q_o and P for each kinetic series at a number of fixed values of r_e

experimental code; g_k[1]		fixed values of r_e					
		0.60	0.65	0.70	0.75	0.80	0.85
A	r_v	1.0751	1.2231	1.3711	1.5192	1.6673	1.8155
	q_o	1.9978	1.9976	1.9974	1.9972	1.9970	1.9969
g_1 = 32	P	65.57	65.93	66.27	66.60	66.92	67.22
B	r_v	1.4211	1.4503	1.4794	1.5086	1.5378	1.5670
	q_o	0.3624	0.3624	0.3623	0.3623	0.3623	0.3623
g_2 = 21	P	59.05	58.91	58.78	58.66	58.56	58.47
C	r_v	—	1.1237	1.3192	1.5147	1.7102	1.9058
	q_o	—	2.7371	2.7370	2.7370	2.7369	2.7369
g_3 = 22	P	—	18.11	18.05	18.00	17.95	17.91
D	r_v	1.3266	1.3946	1.4627	1.5308	1.5989	1.6671
	q_o	0.8869	0.8868	0.8867	0.8867	0.8866	0.8866
g_4 = 34	P	13.78	13.67	13.57	13.48	13.40	13.33
E	r_v	1.3822	1.4249	1.4676	1.5103	1.5530	1.5957
	q_o	0.5468	0.5467	0.5467	0.5467	0.5466	0.5466
g_5 = 27	P	17.78	17.57	17.38	17.21	17.05	16.90
F	r_v	1.4146	1.4492	1.4838	1.5184	1.5530	1.5876
	q_o	0.4476	0.4476	0.4476	0.4476	0.4476	0.4475
g_6 = 20	P	1.497	1.530	1.563	1.595	1.627	1.659
H	r_v	1.1617	1.2889	1.4161	1.5434	1.6706	1.7979
	q_o	1.7287	1.7287	1.7286	1.7286	1.7286	1.7285
g_7 = 20	P	6.234	6.183	6.138	6.099	6.065	6.034
J	r_v	1.3391	1.4115	1.4838	1.5562	1.6286	1.7010
	q_o	0.9208	0.9207	0.9206	0.9205	0.9204	0.9203
g_8 = 25	P	7.896	7.770	7.666	7.581	7.512	7.458
L	r_v	1.4475	1.4737	1.4998	1.5260	1.5522	1.5784
	q_o	0.3252	0.3252	0.3252	0.3252	0.3252	0.3251
g_9 = 20	P	12.16	11.97	11.79	11.62	11.45	11.30
$\sum_{k=1}^{9} g_k = 221$					200.85[2]		

[1] g_k = number of pairs of input data resulting from the kth experiment

[2] ΣP at $r_e = 0.75$ amounts to 200.85; if the model fits within each kinetic series (see 7.3.3), the sample standard deviation of f_v is $s = \pm\sqrt{\frac{200.85}{221-18}} = \pm 1.0\%$ (conversion)

The F.C.A.-A method is now continued as follows:

- For all kinetic series, which are different in initial monomer feed ratio and total molar concentration, the points with coordinates (r_e, r_v) are plotted in a graph of r_e versus r_v (see Fig. 7-1).

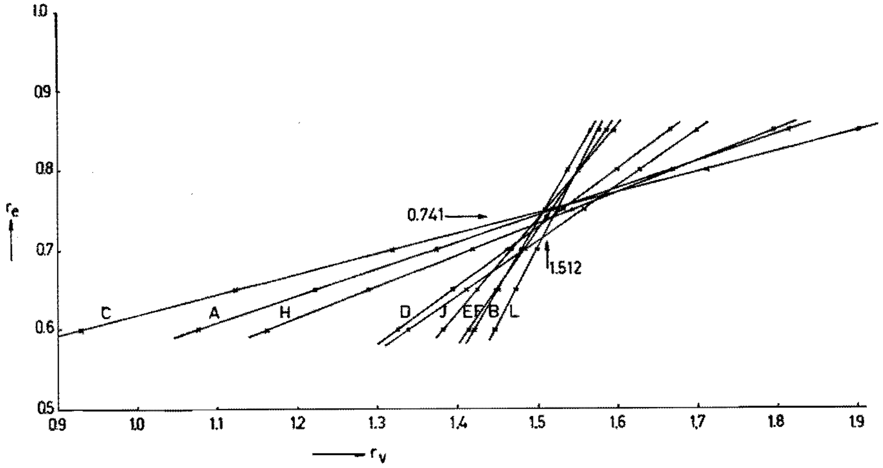


Fig. 7-1 Relations between $\hat{r}_e$ and $\hat{r}_v$ computed by the F.C.A.-A method

- Since the $r_e - r_v$ relations appear to be practically straight lines in the region of interest, linear regression (ref. 6) is applied to determine these lines for each experiment (see Fig. 7-1); the correlation coefficient deviates less than 10^{-4} from unity for any of the lines.
- The centre of gravity of the area defined by the significant intersection points in Fig. 7-1 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 in Fig. 7-1, the errors in $\hat{r}_e$ and $\hat{r}_v$ are estimated. Since the area of significant intersection points is small in comparison with the results of other methods of computation with the same input data (ref. 5), a rather objective choice can be made for the r-values.

The result of the F.C.A.-A method is:

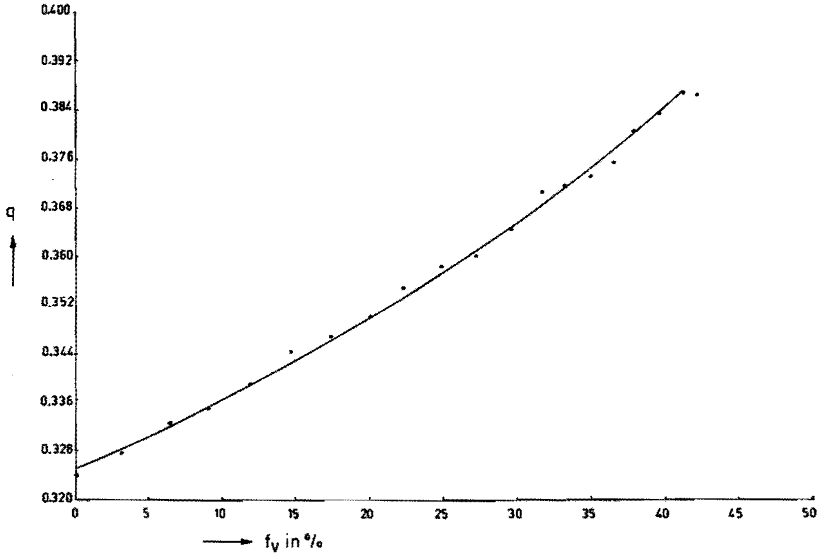
$$\hat{r}_e = 0.741 \pm 0.010$$
$$\hat{r}_v = 1.512 \pm 0.015$$

The error estimates may be caused by the experimental error in the input data (which are assumed to have a normal distribution) as well as by the possible incompetency of the usual copolymerization model to describe the experiments, whereas the mutual contributions are still unknown.

7.3.3 ADEQUACY OF THE REGRESSION CURVES

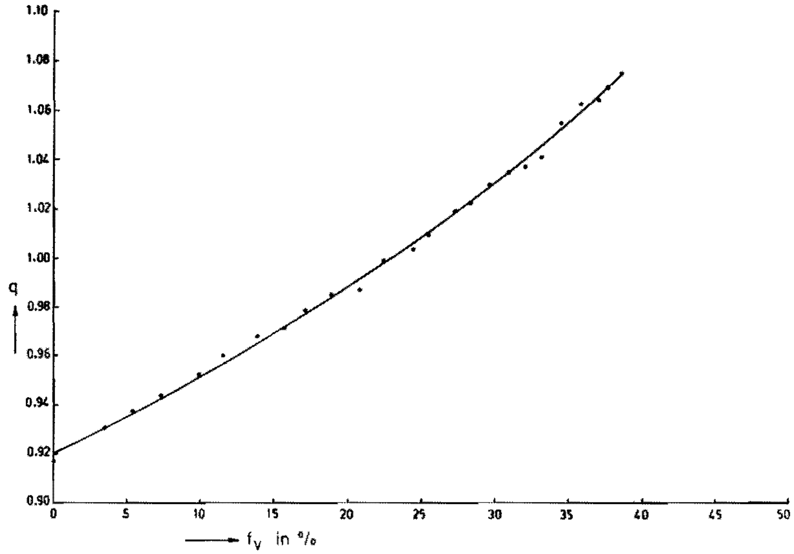
The optimum curve fitting

Since the visual judgement of the quality of the generated "best fitting curve" with regard to the measured points is not easily overemphasized, the curves of the molar feed ratio q versus the degree of conversion f_v are shown in Fig. 7-2 for some

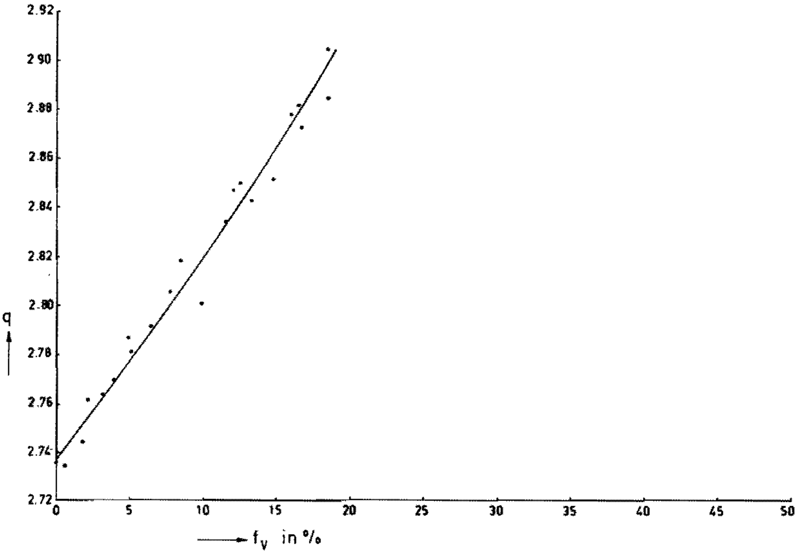


(a)

Fig. 7-2 The molar feed ratio q plotted versus the degree of conversion f_v; regression curves generated by the F.C.A.-A method
(a) experiment L



(b)



(c)

Fig. 7-2 The molar feed ratio q plotted versus the degree of conversion f_v; regression curves generated by the F.C.A.-A method
(b) experiment J
(c) experiment C

representative experiments. The graphs have been drawn for a fixed value of $r_e = 0.75$ and the corresponding computed values of r_v and q_o from Table 7-1. The curves generated for other fixed values of r_e between 0.60 and 0.85 do not visually deviate from these graphs, which is confirmed by the insignificant change in the residual sum of squares (see Table 7-1), and also corresponds with the correlation noticed between $\hat{r}_e$ and $\hat{r}_v$ within one experiment.

At this stage of the investigation it has to be realized that the F.C.A.-A method implies the generation of regression curves of the shape of the copolymerization equation, for each kinetic series in succession. This generation involves the risk of forcing the experimental data into an inappropriate shape *imposed* by the copolymerization model, whereas the latter is to be *tested* in describing the data. However, it can be proved that such a situation does not occur in this investigation:

- Visual inspection of the generated $q - f_v$ relations (of which some representative examples are given in Fig. 7-2) shows that the curves fit the experimental data perfectly for all kinetic series.
- The deviation from the usual model most frequently occurring for other monomer pairs (ref. 7), is non-constancy of the reactivity ratios over the entire range of initial feed compositions. Within each kinetic series, however, the changes in monomer feed composition are comparatively small (see Table 6-2), and consequently the requirement of constancy of the reactivity ratios is readily satisfied. Thus application of the model for regression purposes over a small range of monomer feed compositions, i.e. within each kinetic experiment, seems permissible.
- In chapter 5 (see 5.4) the mean experimental error in the determination of $q = n_e/n_v$ is estimated as ± 0.3%, and for an average conversion of 20% the estimated *absolute* error in the determination of f_v is ± 0.8% (conversion). In the non-linear estimation procedure the sum of the squares of the deviations of f_v is minimized and $q = n_e/n_v$ is assumed to contain no experimental error. But this assumption is not met in the present investigation. The conse-

quences of this simplification can be compensated (at least to a certain extent) by introducing an additional error in f_v of about ± 0.8% (conversion) (calculated with the mean slope of the q versus f_v curves). This results in an approximation of the absolute "modified experimental error" in f_v of 1.6% (conversion).

After the generation of the regression curves of the shape of the copolymerization equation for each experiment separately, the sample standard deviation of f_v for all experiments can be calculated (see Table 7-1) and is ± 1.0% (conversion).

Since the "modified experimental error" in f_v agrees fairly well with the standard deviation derived from the curve fitting procedure, it may be concluded that no measurable error is added by generating regression curves of the shape of the copolymerization equation.

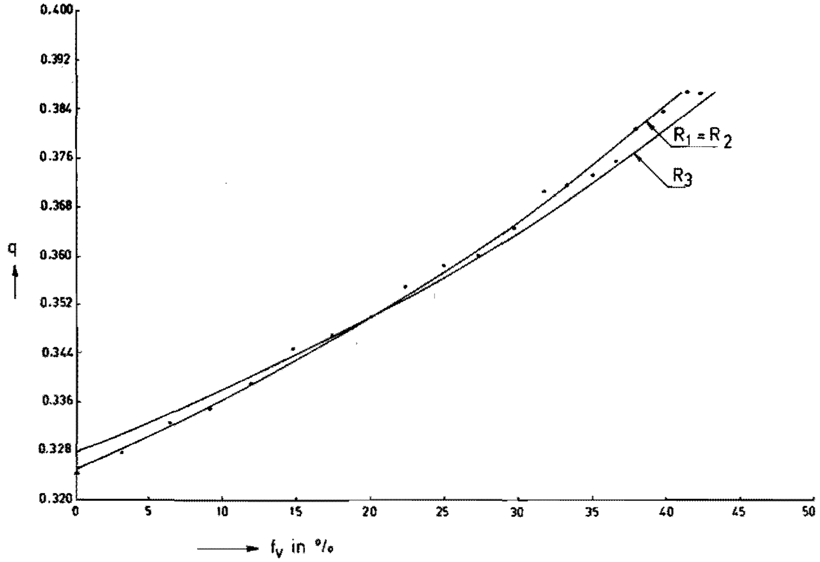
It can be concluded from the above considerations that to the regression curves of q versus f_v generated by the F.C.A.-A method the optimum quality may be assigned, at least at the error level concerned and for relations having some chemical meaning. Thus all error sources, experimental ones as well as those arising from the possible incompetency of the model to describe *all* experiments with the *same* pair of r-values, are represented by the area of intersection points in Fig. 7-1.

The sensitivity of the curve fitting

In order to ascertain the sensitivity of the regression curves to changes in r_e and r_v, the relations between the molar feed ratio $q = n_e/n_v$ and the degree of conversion f_v are recomputed for all experiments. These recomputations (see Table 7-2) are carried out primarily with the r_e and r_v values as determined by the F.C.A.-A method (recomputation mode R_1), and secondly with r_e and r_v values intentionally chosen different from the "best" estimates (recomputation modes R_2 and R_3). Though the adequacy of the model will be proved more extensively in 7.5, the small difference between $\Sigma P_{R1} = 205.4$ (see Table 7-2) and $\Sigma P_A = 200.9$ (see Table 7-1) already indicates that

Table 7-2 Sensitivity to changes in r_e and r_v of the curve fitting; experiments arranged in the order of increasing ethylene content

experimental code; g_k = number of input data	residual sum of the squares of the deviations in f_v		
	recomputation mode R_1; $r_e = 0.74$ $r_v = 1.51$	recomputation mode R_2; $r_e = 0.70$ $r_v = 1.51$	recomputation mode R_3; $r_e = 0.74$ $r_v = 1.43$
L $g_9 = 20$	12.1	12.1	52.7
B $g_2 = 21$	59.0	63.1	91.3
F $g_6 = 20$	1.6	2.6	15.4
E $g_5 = 27$	17.5	23.6	41.0
D $g_4 = 34$	13.6	18.1	36.0
J $g_8 = 25$	10.2	8.8	44.1
H $g_7 = 20$	6.1	9.6	10.4
A $g_1 = 32$	67.0	82.7	70.5
C $g_3 = 22$	18.3	24.9	18.5
$\sum_{k=1}^{9} g_k = 221$	$\Sigma P_{R1} = 205.4$	$\Sigma P_{R2} = 245.5$	$\Sigma P_{R3} = 379.9$



(a)

Fig. 7-3 The sensitivity of $q - f_v$ relations to changes in r_e and r_v
(a) example given for experiment L; recomputation modes R_1, R_2 and R_3

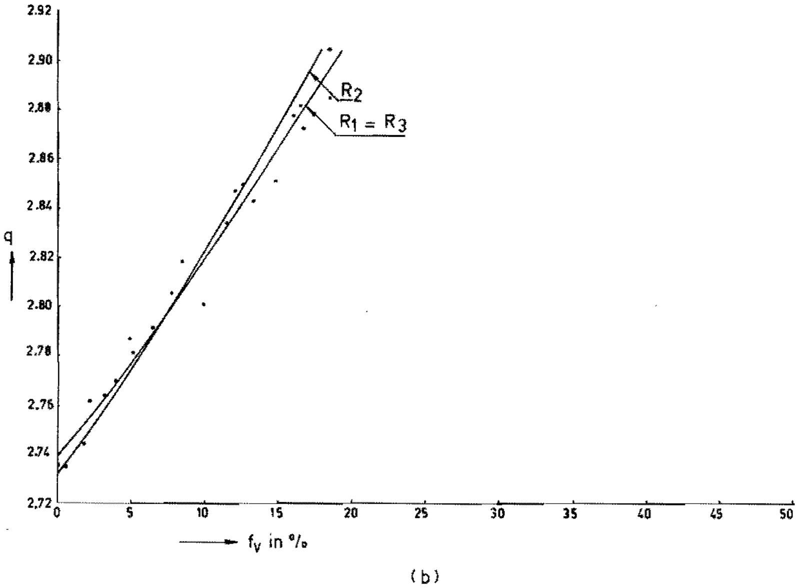


Fig. 7-3 The sensitivity of q - f_v relations to changes in r_e and r_v
(b) example given for experiment C; recomputation modes R_1, R_2 and R_3

recomputation mode R_1 provides an excellent curve fitting for all experiments. Some representative examples of the curve fitting accomplished by the various recomputations are given in Fig. 7-3.

It can be seen from Table 7-2 that a change of 5% in successively r_e and r_v induces in both cases a substantial increase in the total residual sum of squares; Fig. 7-3 shows that these effects become visible in the curve fitting for certain experiments. Additionally, contemplation of Table 7-2 and Fig. 7-3 indicates that the curve fitting for experiments with monomer feed compositions rich in ethylene is sensitive to changes in r_e, whereas the curve fitting for experiments with monomer feed compositions rich in vinylacetate is sensitive to changes in r_v.

7.4 THE F.C.A. METHOD, PROCEDURE B

7.4.1 ESTIMATION OF THE r-VALUES

As already pointed out in 7.2, the r-values may be estimated from the combined results of all kinetic series. The characteristic feature of this method is estimation of the r-values as well as the initial molar feed ratios q_{ok} for all kinetic series simultaneously by minimizing equation (7-3), viz.

$$\sum_{k=1}^{n} \sum_{i=1}^{g_k} F_{ik}^2 \ (r_e, r_v, q_{ok}, q_{ik}, (f_v)_{ik}) \ ,$$

with respect to r_e, r_v and q_{ok} ($k = 1,\ldots\ldots,n$; n = number of experiments). The above minimization procedure immediately leads to the least-squares estimates for r_e, r_v and q_{ok} and the value of the residual sum of squares P. The results are listed in Table 7-3, where also the contributions (P_k) of the various experiments to the residual sum of squares are given.

Table 7-3 Results of the computations according to the F.C.A.-B method

$\hat{r}_e = 0.743 \pm 0.005$[1]
$\hat{r}_v = 1.515 \pm 0.007$[1]

experimental code; g_k[2]	q_{ok}	P_k
A $g_1 = 32$	1.9960	66.9
B $g_2 = 21$	0.3620	59.3
C $g_3 = 22$	2.7358	18.2
D $g_4 = 34$	0.8870	13.6
E $g_5 = 27$	0.5463	17.7
F $g_6 = 20$	0.4475	1.6
H $g_7 = 20$	1.7290	6.1
J $g_8 = 25$	0.9222	10.0
L $g_9 = 20$	0.3254	11.9
$\sum_{k=1}^{9} g_k = 221$		$P_B = 205.3$

1) see 7.4.2 for the computation of the standard deviations

2) g_k = number of pairs of input data resulting from the kth experiment

The curves of the molar feed ratio versus the degree of conversion, with r_e, r_v and q_{ok} from Table 7-3, will not be given since they do not visually deviate from the corresponding graphs generated by the F.C.A.-A method, of which some examples have been given in Fig. 7-2.

7.4.2 COMPUTATION OF THE ERROR IN $\hat{r}_e$ AND $\hat{r}_v$

By an Algol procedure described by Linssen (ref. 8) 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). The procedure yields a matrix which, after multiplication with s^2 (= the sample variance of the input data, see Table 7-1), represents an approximation of the sample variance-covariance matrix of the estimates of the parameters. However, the procedure is only valid under certain conditions, e.g. a normal distribution of the errors, and provides a matrix which is only exactly equal to the sample variance-covariance matrix in case the model is linear in its parameters. Nevertheless, the method is useful if its restrictions are recognized, the more so as no other methods of reasonable simplicity are available.

The resulting approximation of the variance-covariance matrix is:

$$\begin{array}{ccc} & \hat{r}_e & \hat{r}_v \\ \hat{r}_e & 0.28 \times 10^{-4} & 0.30 \times 10^{-4} \\ \hat{r}_v & 0.30 \times 10^{-4} & 0.45 \times 10^{-4} \end{array}$$

Consequently, the estimates and their standard deviations are given by:

$$\hat{r}_e = 0.743 \pm 0.005$$
$$\hat{r}_v = 1.515 \pm 0.007$$

It becomes evident that the agreement with the results of the earlier approximation of the error (see 7.3.2) from the results of the F.C.A.-A method is fairly good, the more so as the error derived from procedure A is an approximation of the 90% confidence intervals, whereas procedure B yields estimates for the standard deviations.

Since the estimation of the error deduced from procedure B implies certain constraints that are associated with the error distribution and the model, and of which it is not easy to verify if they are exactly fulfilled, the somewhat larger errors deduced from procedure A are considered to be the safer approximations of the errors in $\hat{r}_e$ and $\hat{r}_v$.

7.4.3 SHAPE OF THE CONFIDENCE REGIONS

In the preceding error discussions, the confidence intervals of r_e and r_v have been considered, affording separately the estimated errors in $\hat{r}_e$ and $\hat{r}_v$, whereas the consequences of errors in $\hat{r}_e$ and $\hat{r}_v$ occurring simultaneously and the resulting joint confidence limits have not been taken into account. Nevertheless, the joint confidence limits are to be given preference over the perpendicular confidence intervals, since only the former convey the message of which *pairs* of r_e, r_v 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 the confidence regions are reported by Behnken (ref. 4) and Tidwell and Mortimer (ref. 9).

If the r-values are evaluated by a non-linear least-squares method and the sample variance of the input data is known, the procedure permits calculation of the approximate confidence regions under a number of conditions equal to those required for the computation of the sample variance-covariance matrix (see 7.4.2). Since no indications are available to presume that these conditions are severely violated, the procedure is applied to calculate the confidence regions in the present case for the $\hat{r}_e$ and $\hat{r}_v$ determination by the F.C.A.-B method. The results are shown in Fig. 7-4.

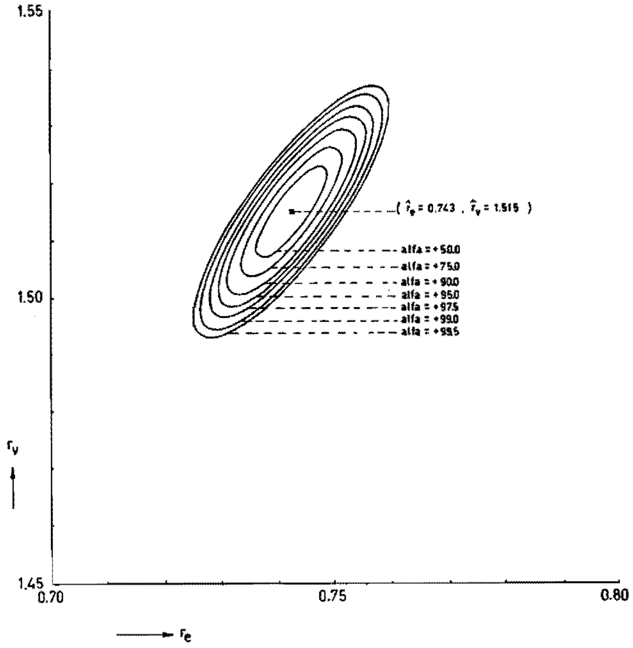


Fig. 7-4 Confidence regions, derived from the F.C.A.-B method; α = probability level

The probability level α, for example α = 90%, means by definition: if a sufficiently large number of complete experimental series are carried out, then in one out of ten cases the (unknown) *actual* pair of *r*-values is situated outside the computed confidence regions.

The shape of the confidence regions emphasizes the importance of considering these regions rather than the perpendicular confidence intervals.

7.5 CONSISTENCY OF THE ALFREY MODEL WITH THE EXPERIMENTAL DATA

The adequacy of the model will be proved by comparing the results of the F.C.A.-A and F.C.A.-B methods.

Before proceeding to outline the adequacy of the model, Table 7-4 has to be explained. In this table, the sum of the squares of the deviations in f_v is tabulated for both regression modes accomplished during the present investigation. Under the heading "regression mode A" are given the results of the F.C.A.-A method (each experiment treated separately) and under "regression mode B" those of the F.C.A.-B method (all experiments treated simultaneously). For ease of survey the experiments are arranged in the order of increasing initial molar feed ratio $q = n_e/n_v$.

Table 7-4 Quality of the curve fittings, provided by both regression modes used, in terms of the residual sum of squares

experimental code;	residual sum of the squares of the deviations in f_v	
g_k = number of input data	regression mode A	regression mode B
L $g_9 = 20$	11.6	11.9
B $g_2 = 21$	58.7	59.3
F $g_6 = 20$	1.6	1.6
E $g_5 = 27$	17.2	17.7
D $g_4 = 34$	13.5	13.6
J $g_8 = 25$	7.6	10.0
H $g_7 = 20$	6.1	6.1
A $g_1 = 32$	66.6	66.9
C $g_3 = 22$	18.0	18.2
$\sum_{k=1}^{9} g_k = 221$	$\Sigma P_A = 200.9$	$P_B = 205.3$

It has been shown in 7.3.3 that the curve fitting accomplished by the F.C.A.-A method (see regression mode A) may be assigned the optimum quality, at least for a q versus f_v relation having some chemical meaning.

Now, if consistency of the model with the experimental data exists, there must be *one* pair of r-values which affords a proper fit of the $q - f_v$ relations with the experimental data for *all* experiments. Consequently, for each experiment the fit obtained with the r-values computed by the F.C.A.-B method can in that case not differ significantly from the fit obtained by the F.C.A.-A method. This means that the quantities ΣP_A and P_B cannot differ significantly either. From Table 7-4 it becomes evident that the differences mentioned are indeed very small. In order to give an impression of the significance of the difference between $\Sigma P_A = 200.9$ and $P_B = 205.3$, it may be stated that in regression mode A a similar difference might already be brought about by 2 of the 221 experimental data exhibiting a deviation of twice the average deviation. Additionally, it has been described in 7.4.1 that regression mode B yields curves which visually coincide with those afforded by regression mode A.

From the above arguments it may be concluded that the Alfrey model for the description of radical copolymerization is completely supported by the data obtained in this investigation within the limits imposed by the experimental error. Since the constancy of the r-values within the experimental error is proved, there are no reasons for extending the model, taking into account penultimate effects or anomalous addition reactions (see 2.2).

7.6 CONCLUSION

The agreement between the results of both computational procedures to determine r-values is very good, which provides supporting evidence to the determination of the monomer reactivity ratios.

The F.C.A.-A method is to some extent related to the usual "intersection method" (see 3.1), since $r_e - r_v$ relations are generated for each kinetic series separately. The determination of the r-values by this method is a slightly subjective procedure.

In contrast to method A, method B provides a unique pair of r-values for a given set of experimental data. In addition, this method allows, though under certain restrictions, calculation of the error in the resulting estimates in terms of either the perpendicular confidence intervals or the joint confidence limits.

The adequacy of the Alfrey model can be proved by comparing the results of the F.C.A.-A and F.C.A.-B methods.

The kinetic implications of the reported results will be discussed in chapter 8.

REFERENCES

1 C.F. Braakman, *Internal Reports Eindhoven University of Technology*, Polymer Technology Section, (1969 and 1970).

2 F.A. Lootsma, *Thesis Eindhoven University of Technology*, (1970).

3 H.O. Hartley, *Technometrics*, 3 (1961) 269.

4 D.W. Behnken, *J. Polymer Sci. A*, 2 (1964) 645.

5 R.L. Hené, *Internal Report Eindhoven University of Technology*, Polymer Technology Section, (1969).

6 *Program Library Hewlett-Packard Calculator Model 9100 A*, (1969) 09100-70818.

7 F.E. Brown and G.E. Ham, *J. Polymer Sci. A*, 2 (1964) 3623.

8 H.N. Linssen, *Internal Report Eindhoven University of Technology*, Department of Mathematics, (1970).

9 P.W. Tidwell and G.A. Mortimer, *J. Polymer Sci. A*, 3 (1965) 369.

CHAPTER 8

DISCUSSION OF THE RESULTS AND CONCLUSIONS

8.1 IMPLICATIONS OF THE RESULTS

The reactivity ratios

In chapter 7 the r-values have been determined as:

$$r_e = \frac{k_{ee}}{k_{ev}} = 0.74 \quad \text{and} \quad r_v = \frac{k_{vv}}{k_{ve}} = 1.51$$

Since $k_{ev}/k_{ee} = 1.35$ and $k_{vv}/k_{ve} = 1.51$, it appears that, if vinylacetate and ethylene compete for the same free radical, vinylacetate will exhibit a higher reactivity than ethylene, comparatively independently of the type of free radical involved. As a consequence, vinylacetate will be built in to a relatively greater extent. This feature is in agreement with the feeling that a given free radical will have the tendency to add preferably that monomer (viz. vinylacetate) that affords the free radical with the greater extent of stabilization by resonance.

In addition, the vinylacetate radical chain end, being the more stable radical, can be expected to show less reactivity than the ethylene radical chain end, and so $k_{ev} > k_{vv}$ as well as $k_{ee} > k_{ve}$. However, the type of copolymerization experiments considered in this investigation can only provide the ratios of propagation constants r_e and r_v and do not reveal the individual values of the various propagation constants.

Fig. 8-1 shows for the r-values determined in the present investigation the composition of the instantaneously formed copolymer as a function of the monomer feed composition.

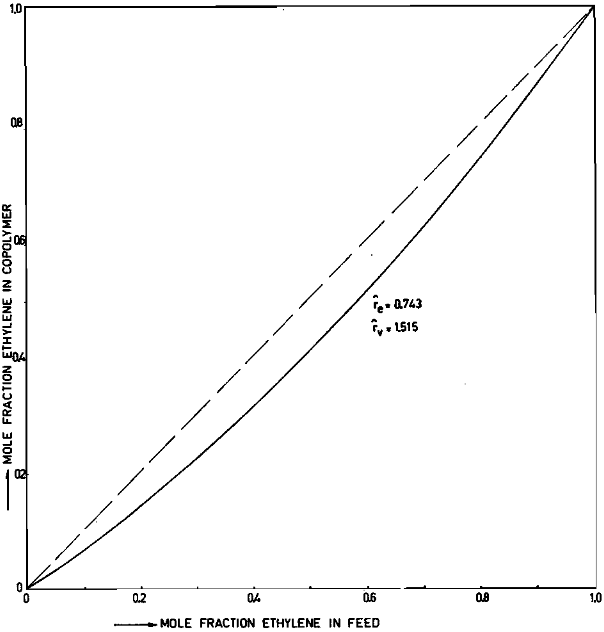


Fig. 8-1 Instantaneous copolymer composition as a function of monomer feed composition

The product of reactivity ratios

The product of the reactivity ratios $\pi = k_{ee}k_{vv}/k_{ev}k_{ve} = 1.12$, being larger than unity, indicates a slight tendency towards homopolymerization (see 2.4).

For instance, in the case of a 1:1 copolymer the number-average sequence length can be derived from equations (2-7), (2-8), (2-10) and (2-11) and is equal to $\bar{n}_e = \bar{n}_v = 1 + \sqrt{r_e r_v} = 2.06$. Also, consideration of this number-average sequence length shows that the copolymers concerned are distributed in a somewhat blockier fashion than the random distribution would predict in virtue of the ideal copolymerization behaviour (viz. $r_e r_v = 1$). The differences are, however, very small and even high resolution NMR techniques will not be capable (ref. 1) of revealing such slight deviations from the ideal sequence length distribution.

In accordance with the conclusion reached in 2.5, it can be stated that the *Q-e* scheme is unable to describe the copolymerization of ethylene and vinylacetate under the relevant conditions since $\pi > 1$.

The adequacy of the Alfrey model

In 7.5 it has been proved that the Alfrey model is consistent with the experimental data obtained in this investigation.

The constancy of the monomer reactivity ratios implies:

- r_e and r_v are independent of the monomer feed composition varying from 24-74 mole % ethylene, the total monomer concentration between 0.91 and 2.85 mole/dm^3, and the composition of the resulting copolymer (see Table 6-2 and Fig. 6-1);
- r_e and r_v are independent of the copolymer concentration in the reaction mixture varying from 0 to 62 g/dm^3 (see Table 6-2);
- r_e and r_v are constants regardless of the degree of polymerization for the products of all experiments, in the range $\overline{D.P.}$ = 420 - 870 (see Table 6-1);
- penultimate effects (see 2.2) play no part and anomalous addition reactions (see 2.2) do not noticeably take place.

A discussion of these implications follows here.

The monomer reactivity ratios, which are ratios of propagation constants, appear to be independent of environmental changes within the region pertinent to investigation. In the case of uncharged molecules it seems probable that the reaction rates are independent of, or at least equally influenced by, the reaction medium. The law of mass action seems to hold here.

Despite the high copolymer concentrations attained in various experiments and the resulting high viscosities of the reaction medium, it is unlikely that diffusion control will have taken place. Comparison of Tables 6-1 and 6-2 reveals that no tendency can be found towards an exceptionally large $\overline{D.P.}$ for the products from those experiments attaining high copolymer end concentrations. This means that the termination reactions are not noticeably diffusion controlled. In this train of thought it is most unlikely that the propagation rate constants will be diffusion controlled. Even in the case that the propagation steps were influenced to some extent by the low diffusion rates of large growing molecules, k_{ee} and k_{ev} as well as k_{vv} and k_{ve} would be approximately equally influenced as they pertain to the same polymer molecule. Consequently, the r-values will not be affected.

It may occur that $\overline{D.P.}$ is predominantly determined by chain transfer to small molecules. But then the reasoning of the preceding paragraph also holds. In addition, comparison with data collected by Flory (ref. 2) shows that the present copolymer concentrations are very low with respect to the region where diffusion controlled propagation steps generally occur.

Table 6-1 shows that $\overline{D.P.}$ decreases as the ethylene content increases. This indicates that either the type of termination reaction or the limiting effect of chain transfer on $\overline{D.P.}$, depends on the ethylene content. The latter alternative is preferred as it is in accordance with data from Wiley et al. (ref. 3). They report that in the radical polymerization of ethylene at low pressure $\overline{D.P.}$ is governed by chain transfer to monomer.

Apparently the degree of polymerization is sufficiently high to neglect initiation and termination steps with respect to the propagation steps as is assumed in the derivation of the copolymerization equation used. This is obvious when it is realized that at the lowest average value of the degree of polymerization (see Table 6-1) initiation and termination contribute for only 0.5% to monomer conversion.

Since the r-values have been shown to be constants over the range of monomer feed composition covered by the experiments, penultimate effects or anomalous addition reactions do not disturb the fitting of the curves (see 7.5). This does not mean, however, that e.g. anomalous addition does not occur in ethylene-vinylacetate copolymerization under the relevant conditions. But in virtue of the results of this investigation it cannot be decided whether anomalous addition occurs either only rarely (or not at all) or more often with a rate constant only slightly different from that of the normal addition.

8.2 ESTIMATED EFFECT OF PRESSURE AND TEMPERATURE ON THE MONOMER REACTIVITY RATIOS

Although the determination of the influence of pressure and temperature on the reactivity ratios is beyond the scope of this thesis, an approximate indication of the pressure and temperature effects to be expected will be given. On the one hand, this may facilitate the comparison of the results achieved in this investigation with the diversity of data in the literature. On the other hand, as for the pressure influence, the present results will provide a basis for future research on the effect of pressure on the reactivity ratios in ethylene-vinylacetate copolymerization. As a consequence, it seems useful to point out the pattern to be expected.

8.2.1 EFFECT OF PRESSURE

The pressure dependence of the monomer reactivity ratios is governed by the difference between the volume of activation for the homopropagation and the crosspropagation reactions (ref. 4):

$$\frac{\partial \ln r_e}{\partial p} = - \frac{\Delta V_{ee}^{\#} - \Delta V_{ev}^{\#}}{RT}$$

or

$$(r_e)_{p_2} = (r_e)_{p_1} \exp\left\{ -\left(\frac{\Delta V_{ee}^{\#} - \Delta V_{ev}^{\#}}{RT} \right)(p_2 - p_1) \right\} \tag{8-1}$$

where the activating volume $\Delta V_{ee}^{\#}$ is the partial molar volume of the transition state $V_{ee}^{\#}$ minus the sum of the partial molar volumes of the reactants $(V_{e\cdot} + V_e)$.

Consequently:

$$\Delta V_{ee}^{\#} - \Delta V_{ev}^{\#} = (V_{ee}^{\#} - V_{ev}^{\#}) - (V_e - V_v) = A \tag{8-2}$$

The analogous expression for r_v is:

$$(r_v)_{p_2} = (r_v)_{p_1} \exp\left\{-\left(\frac{\Delta V_{vv}^{\#} - \Delta V_{ve}^{\#}}{RT}\right)(p_2 - p_1)\right\} \tag{8-3}$$

with $$\Delta V_{vv}^{\#} - \Delta V_{ve}^{\#} = (V_{vv}^{\#} - V_{ve}^{\#}) - (V_v - V_e) = B \tag{8-4}$$

Combination of equations (8-1), (8-2), (8-3) and (8-4) gives:

$$(r_e r_v)_{p_2} = (r_e r_v)_{p_1} \exp\left\{-\left(\frac{A + B}{RT}\right)(p_2 - p_1)\right\} \tag{8-5}$$

The effect of pressure on the reactivity ratios has been summarized by Weale (ref. 4) for many copolymerization reactions (except ethylene-vinylacetate). His tabulations show that the product of the reactivity ratios tends to approach unity as pressure increases, whereas no clear patterns appear for the influence of pressure on the individual *r*-values. Apparently the copolymerization moves to the ideal behaviour and the free radicals lose their individual selectivity with increasing pressure.

Making an attempt to approximate the influence of pressure on ethylene-vinylacetate copolymerization, it can be assumed as a first approximation that:

$$\Delta V_{ee}^{\#} - \Delta V_{ev}^{\#} \simeq -(\Delta V_{vv}^{\#} - \Delta V_{ve}^{\#}) \tag{8-6}$$

This means that the volumetric contributions of radicals and monomers to the volume of the different transition states are independent of the kind of transition state formed. If equation

(8-6) holds, the r-values will, according to equations (8-1), (8-3) and (8-5), change with increasing pressure in opposite directions with $r_e r_v$ = constant. Under the less stringent condition of $(\Delta V_{ee}^{\#} - \Delta V_{ev}^{\#})$ and $(\Delta V_{vv}^{\#} - \Delta V_{ve}^{\#})$ exhibiting only opposite signs, it can be stated that with increasing pressure the r-values will still change in opposite directions, though at different rates. Whether they will tend to converge or to diverge, depends on the magnitude of the activating volumes of the homopropagation and the crosspropagation steps. When r_e and r_v move both towards unity with increasing pressure, as is suggested by the literature cited in Table 2-1, r_e will increase and r_v will decrease, which leads to the deduction $\Delta V_{ee}^{\#} < \Delta V_{ev}^{\#}$ and $\Delta V_{vv}^{\#} > \Delta V_{ve}^{\#}$. Since the activating volumes under consideration are negative (ref. 4), the above would suggest that on the coming into being of the transition state the contraction of the reactants is smaller when the vinylacetate monomer or radical is involved than in the case of the ethylene monomer or radical.

The numerical value of the effect of pressure on the r-values may be estimated as follows. According to (ref. 4) the activating volumes for a number of well-known free-radical, liquid phase homopolymerization reactions vary from approximately -15 to -25 cm^3/mole. A reasonable approximation of the order of magnitude of the difference between the volume of activation for a homopropagation and a crosspropagation step seems to be 5 cm^3/mole. In this case the r_e-value at 1000 kgf/cm^2 and 62°C would be (equation (8-1)):

$$(r_e)_{1000} \simeq 0.89$$

and the r_v-value (equation (8-3)):

$$(r_v)_{1000} \simeq 1.26$$

Thus the pressure effect on the reactivity ratios may be expected to be approximately 20%/1000 kgf/cm^2.

8.2.2 EFFECT OF TEMPERATURE

Starting from the theory of the transition state, the reactivity ratio r_e may be expressed as:

$$r_e = \frac{k_{ee}}{k_{ev}} = \exp\left\{\frac{-(\Delta H_{ee}^{\#} - \Delta H_{ev}^{\#})}{RT} + \frac{\Delta S_{ee}^{\#} - \Delta S_{ev}^{\#}}{R}\right\}$$

A similar expression can be derived for r_v.

$\Delta H_{ee}^{\#}$, $\Delta H_{ev}^{\#}$, $\Delta S_{ee}^{\#}$ and $\Delta S_{ev}^{\#}$ are successively the heats of activation and entropies of activation for the reactions of the ethylene radical with ethylene and vinylacetate monomer molecules.

Terteryan, Dintses and Rysakow (ref. 5) report r_e-values at 70°C and 130°C, with which they arrive at:

$$\Delta H_{ee}^{\#} - \Delta H_{ev}^{\#} = 1058 \text{ cal/mole}$$

$$\Delta S_{ee}^{\#} - \Delta S_{ev}^{\#} = 2.56 \text{ cal/mole } ^{\circ}\text{C}$$

These data permit the calculation of r_e-values at various temperature levels or conversion of the data reported at different temperatures (see Table 2-1) to 62°C using the following equation:

$$(r_e)_{T_2} = (r_e)_{T_1} \exp\left\{\frac{\Delta H_{ee}^{\#} - \Delta H_{ev}^{\#}}{R}\right\}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

The results are given in Table 8-1 (see 8.3). It appears from Table 8-1 that, although the pressure influence is left out of consideration, the value of $\Delta H_{ee}^{\#} - \Delta H_{ev}^{\#} = 1058$ cal/mole may account for the effect of temperature on the majority of the reported r_e-values.

The r_v-values reported by the authors referred to (ref. 5) do not depend on temperature in the range from 70-130°C. This behaviour would suggest:

$$\Delta H_{vv}{}^{\#} - \Delta H_{ve}{}^{\#} \simeq 0$$

However, this statement is probably not based on a sound experimental footing. In 8.3 it will be shown that particularly the r_v-values reported in the literature are the less reliable ones.

It may be concluded that the effect of temperature on r_e can be adequately described, whereas the temperature effect on r_v is less comprehensible. This should be a useful subject for future investigation.

8.3 COMPARISON OF THE RESULTS OF THIS INVESTIGATION WITH OTHER DATA

Comparison of the r_e-values

The r_e-values reported in the literature at various temperatures (see Table 2-1) have been converted to 62°C by the procedure described in 8.2.2. The results are listed in Table 8-1.

Table 8-1 Conversion to 62°C of the r_e-values, reported by various investigators at different temperatures

sources	r_e reported	temperature °C	pressure kgf/cm^2	r_e converted 1)
Burkhart and Zutty (ref.6)	1.07	90	1000	0.95
Terteryan et al. (ref.5)	0.77	70	400	0.74
Terteryan et al. (ref.5)	0.97	130	400	0.74
Brown and Ham (ref.7)	1.01	150	840	0.73
Erussalimsky et al. (ref.8)	0.16	60	100	0.16
Erussalimsky et al. (ref.8)	0.70	60	1200	0.71
This investigation (ch.7)	0.74	62	35	0.74

1) r_e is converted to 62°C, but uncorrected for pressure differences

In the given tabulation the r_e-values have not been corrected for the differences in pressure. Since the conversion of r_e is based on data found by Terteryan et al. measured at 400 kgf/cm^2, being approximately the average experimental condition, the correction is believed to be comparatively small (see also

8.2.1). Furthermore, it seems questionable whether it is significant to consider both temperature and pressure effects on r_e as additive independent corrections.

Omitting the strongly deviating result of Erussalimsky et al., it may be concluded that the r_e-value determined in this investigation shows, after temperature correction, a good agreement with the r_e-values found in the literature, particularly with those reported by Terteryan et al. and by Brown and Ham.

Comparison of the r_v-values

Contemplation of the r_v-values in Table 2-1 (omitting again the r_v-values reported by Erussalimsky et al. and the r_v-value from this investigation) gives rise to the feeling that the reported r_v-values are neither temperature nor pressure dependent in the regions concerned. Notwithstanding this, the present investigation yields an r_v-value which is significantly different from the other reported values. The discrepancy is such that it cannot readily be explained from the fact that previous investigators applied less advanced analytical and computational methods. So one is inclined to suppose that the r_v-values from the quoted literature are severely biased by deviating reaction conditions, particularly liquid phase separation and/or precipitation of copolymer.

It has been stated in 2.6.1 that in carrying out high-pressure copolymerizations one should be constantly on one's guard for pressure-induced phase and solubility changes. An extreme example of this effect is found in the report that gases widely different in polarity may become partially immiscible at high pressures even though they are above their critical temperatures (ref. 9). The risk of precipitation also actually exists, since benzene or toluene (used as solvents in some of the quoted investigations) are poorer solvents than *tert*-butylalcohol (used as solvent in the present investigation), especially for the copolymers with high vinylacetate content (see 1.4).

An explanation of the deviating r_v-values in the literature quoted might be the inclusion of the monomer feed mixture by precipitating copolymer and the subsequent diffusion controlled vinylacetate addition reactions. The diffusion limitation, affecting the propagation reactions:

$$\sim e\cdot + v \xrightarrow{k_{ev}} \sim v\cdot \quad \text{and}$$

$$\sim v\cdot + v \xrightarrow{k_{vv}} \sim v\cdot \quad ,$$

thus tends to increase $r_e = k_{ee}/k_{ev}$ and to decrease $r_v = k_{vv}/k_{ve}$. However, it has been shown in 7.3.3 (see also Table 7-2 and Fig. 7-3) that the results of experiments starting from those monomer feed compositions that are richer in vinylacetate determine r_v to a greater extent than they do r_e. Since precipitation of copolymer is only expected to occur during these experiments, the result of all experiments covering a wide and approximately symmetrical range of monomer feed composition might very well be a good r_e-value and too low an r_v-value.

Unfortunately, the relative literature provides too little supplementary information on the reaction conditions to treat this problem more thoroughly. Only more extensive model tests, as accomplished during this investigation, and a study of the phase behaviour under the conditions of the literature quoted, might lead to an explanation of this discrepancy.

Estimation of the *r*-values from *Q*-*e* data

Finally an indirect approximation of the *r*-values of the ethylene-vinylacetate system with data obtained from the literature provides a reasonable agreement for r_e as well as r_v.

Terteryan, Braudo and Dintses (ref. 10) have reported a survey of the results of the copolymerization of ethylene with the comonomers vinylchloride, vinylfluoride, tetrafluoroethylene and *n*-butyl acrylate. With the reported values of the reactivity ratios (of which the products are all < 1), and the *Q* and *e* values for the comonomers taken from Young's tabulation (ref. 11), the Q_e and e_e values for ethylene can be calculated (see equations (2-19) and (2-20)), for each ethylene-comonomer pair. The resulting mean values $\overline{Q}_e$ and $\overline{e}_e$ are:

$\overline{Q}_e = 0.018$

$\overline{e}_e = -0.093$ under the average experimental conditions of 100°C and 700 kgf/cm^2.

From these mean values $\overline{Q}_e$ and $\overline{e}_e$, together with the Q_v and e_v values for vinylacetate taken from Young's summary (ref. 11):

$Q_v = 0.026$

$e_v = -0.22$ at 60-70°C and atmospheric pressure,

the r-values for the ethylene-vinylacetate system can be calculated (see equations (2-19) and (2-20)) to be:

$r_e = 0.69$

$r_v = 1.42$,

whereas this investigation yields:

$r_e = 0.74$

$r_v = 1.51$ at 62°C and 35 kgf/cm^2.

Logically, the Q-e scheme will never predict values of $r_e r_v > 1$. But, though the application of the Q-e scheme is subject to this constraint (see 2.5) and the reaction conditions are not quite comparable, it may be concluded that the preceding approximation confirms the order of magnitude of the r-values determined in this investigation.

8.4 CONCLUSIONS IN VIEW OF THE AIM OF THE INVESTIGATION

- In behalf of the study of copolymerization reactions dealing with gaseous and/or liquid monomers under pressure, a new and generally applicable experimental method has been developed for pressures from atmospheric to 40 kgf/cm^2; the copolymerization reactions are followed in detail by frequent sampling from the reactor and subsequent compositional analysis of the reaction mixtures by means of quantitative gas-liquid chromatography (see chapters 4 and 5).
- This method allows of a more justified and accurate determination of the monomer reactivity ratios than other methods commonly used (see chapters 3, 4 and 7).
- In the study of the copolymerization reaction of ethylene with vinylacetate in the liquid phase at 62°C and 35 kgf/cm^2 this method has been applied successfully (see chapter 6).
- Even at pressures as low as 35 kgf/cm^2, in the liquid phase at 62°C and by free-radical initiation, high molecular weight copolymers of ethylene and vinylacetate can be prepared over a wide composition range (18-70 mole % ethylene).

  A study of the phase behaviour reveals that under the conditions mentioned the reaction mixture is a homogeneous single phase system throughout all experiments (see chapter 6).
- The monomer reactivity ratios have been determined by computational procedures based on non-linear least-squares methods.

  For the free-radical solution copolymerization of ethylene with vinylacetate, in *tert*-butylalcohol at 62°C and 35 kgf/cm^2, the monomer reactivity ratios are (see chapter 7):

$$\hat{r}_e = 0.743 \pm 0.010$$

$$\hat{r}_v = 1.515 \pm 0.015$$

- Under the relevant conditions the copolymerization of ethylene with vinylacetate can be accurately and adequately described by the Alfrey model within the narrow limits imposed by the experimental error. No reasons are available to extend the model, taking into account penultimate effects or anomalous addition reactions (see chapter 7).
- In the copolymer chains the monomers will be distributed in a somewhat blockier fashion than the random distribution would predict in virtue of the ideal copolymerization behaviour (see chapter 8).

REFERENCES

1 T.K. Wu, *J. Polymer Sci. A-2*, 8 (1970) 167.
2 P.J. Flory, *Principles of Polymer Chemistry*, (1964) 125, Cornell University Press, New York.
3 R.H. Wiley, N.T. Lipscomb, F.J. Johnston and J.E. Guillet, *J. Polymer Sci.*, 57 (1962) 867.
4 K.E. Weale, *Chemical Reactions at High Pressures*, (1967) chapter 8, E. & F.N. Spon Ltd., London.
5 R.A. Terteryan, A.I. Dintses and M.V. Rysakow, *Neftekhimiya*, 3 (1963) 719.
6 R.D. Burkhart and N.L. Zutty, *J. Polymer Sci. A*, 1 (1963) 1137.
7 F.E. Brown and G.E. Ham, *J. Polymer Sci. A*, 2 (1964) 3623.
8 B. Erussalimsky, N. Tumarkin, F. Duntoff, S. Lyubetzky and A. Goldenberg, *Makromol. Chem.*, 104 (1967) 288.
9 D.S. Tsiklis, *Doklady Akad. Nauk S.S.S.R.*, 86 (1952) 1159.
10 R.A. Terteryan, E.E. Braudo and A.I. Dintses, *Russ. Chem. Rev.*, 34 (1965) 290.
11 L.J. Young, *J. Polymer Sci.*, 54 (1961) 411.

SUMMARY

Although the free-radical copolymerization of ethylene with vinylacetate has been known since 1938, the copolymerization behaviour has never been investigated thoroughly. The values of the monomer reactivity ratios (r-values) reported in the literature are contradictory and unsurveyable, and probably depend on the often unknown reaction conditions under high pressure. In addition, the procedures generally used to study copolymerization reactions are deficient in determining r-values with sufficient accuracy and in model testing, particularly in the case of more complicated reaction conditions (e.g. pressure and gaseous monomers).

In behalf of a detailed study on the course of copolymerization reactions, this thesis describes an improved and generally applicable experimental method and an efficient computational procedure to match.

The experimental method is based on quantitative gas chromatography, and permits frequent measurement of the monomer feed composition throughout copolymerization or polymerization processes at pressures up to 40 kgf/cm^2. A reaction vessel, designed for the purpose, guarantees the absence of a gas phase, operation at constant pressure, and easy representative sampling. A highly accurate analytical system is developed, consisting of a sampling device operating at pressures up to 40 kgf/cm^2, a specially adapted, extremely stable gas chromatograph, and an electronic integrator.

The method under consideration is applied to the study of the copolymerization reaction of ethylene with vinylacetate in a series of kinetic experiments in which a relatively high degree of conversion is reached. It is shown that the radical initiated copolymerization of ethylene and vinylacetate does not necessarily require high pressure. At a pressure of 35 kgf/cm^2, in the liquid phase at 62°C and under the influence of a free-radical initiator, copolymers of fairly high molecular weight are prepared containing 18-70 mole % ethylene. A number of preliminary experiments reveal the phase behaviour of the reaction mixture.

In order to determine the reactivity ratios and to verify the validity of the Alfrey model, the parameters becoming experimentally accessible, i.e. monomer feed composition and degree of conversion, are entered into two different computational procedures. Both computational procedures are based on non-linear least-squares methods applied to the integrated version of Alfrey's copolymerization equation.

The first method of computation is to some extent related to the classical way of determining r-values, on the understanding that for each kinetic series separately, curves are generated in the $r_e - r_v$ plane. The determination of the best fitting r-values by this method appears to be a slightly subjective practice.

The second method of computation allows of calculating the r-values from the combined data of all kinetic series simultaneously. The main advantage of this procedure is that it provides a unique pair of r-values for a given set of experimental data. With certain restrictions, this method admits of calculating the error in the resulting r-values in terms of the joint confidence limits.

It is shown that the experimental data are consistent with the Alfrey model; the r-values are determined accurately. For the free-radical copolymerization of ethylene and vinylacetate in solution (*tert*-butylalcohol) at 62°C and 35 kgf/cm^2,

$$r_e = 0.743 \pm 0.010$$

and

$$r_v = 1.515 \pm 0.015 \; .$$

The implications of the results are discussed. It appears that the copolymerization reaction of ethylene and vinylacetate, under the relevant conditions, is unexpectedly well described by the Alfrey model. The resulting r_e-value shows a reasonable agreement with some of the data reported in the literature; the resulting r_v-value, however, is quite different from any of the data found in the literature. It is suggested that the discrepancy can be interpreted by unnoticed inhomogeneity of the reaction phase in the high-pressure process, commonly applied by other investigators.

SAMENVATTING

Ofschoon de radicaal copolymerisatie van etheen en vinylacetaat reeds sinds 1938 bekend is, is het copolymerisatiegedrag nooit grondig onderzocht. De gepubliceerde waarden van de reactiviteitsverhoudingen van de monomeren (*r*-waarden) zijn tegenstrijdig en onoverzichtelijk, en hangen waarschijnlijk af van de veelal onbekende reactiecondities onder hoge druk. Bovendien schieten de procedures die gewoonlijk gebruikt worden voor de bestudering van copolymerisatiereacties tekort in een voldoende nauwkeurige bepaling van de *r*-waarden en in het uitvoeren van een modeltest, in het bijzonder in geval van meer gecompliceerde reactiecondities (bijv. druk en gasvormige monomeren).

Ten behoeve van een gedetailleerd onderzoek naar het verloop van copolymerisatiereacties, wordt in dit proefschrift een verbeterde en algemeen toepasbare experimentele methode beschreven en een daarbij aansluitende doelmatige berekeningsprocedure.

De experimentele methode berust op quantitatieve gaschromatografie en voorziet in de mogelijkheid tot veelvuldige bepaling van de monomere voedingssamenstelling gedurende copolymerisatie- of polymerisatieprocessen bij drukken tot 40 kg/cm^2. Een reactievat dat voor dit doel is ontworpen, waarborgt de afwezigheid van een gasfase, werking bij constante druk en gemakkelijke representatieve monstername. Een zeer nauwkeurig analytisch systeem is ontwikkeld, bestaande uit een monstername-apparaat dat werkt bij drukken tot 40 kg/cm^2, een speciaal aangepaste, uiterst stabiele gaschromatograaf en een electronische integrator.

De onderhavige methode wordt toegepast bij de bestudering van de copolymerisatiereactie van etheen en vinylacetaat in een reeks kinetische experimenten waarbij een betrekkelijk hoge omzettingsgraad wordt bereikt. Aangetoond wordt dat de door radicalen geïnitieerde copolymerisatie van etheen en vinylacetaat niet noodzakelijk een hoge druk vereist. Bij een druk van 35 kg/cm^2, in de vloeibare fase bij 62°C en onder invloed van een radicaal initiator, zijn copolymeren van tamelijk hoog molecuulgewicht bereid die 18-70 mol % etheen bevatten. Een aantal inleidende experimenten toont het fasegedrag van het reactiemengsel.

Teneinde de reactiviteitsverhoudingen te bepalen en het Alfrey model op zijn geldigheid te testen, fungeren de nu experimenteel toegankelijke parameters (monomere voedingssamenstelling en omzettingsgraad) als ingangsgegevens voor twee verschillende berekeningsprocedures. Beide berekeningsprocedures berusten op niet-lineaire methoden der kleinste kwadraten toegepast op de geïntegreerde vorm van de copolymerisatievergelijking volgens Alfrey.

De eerste berekeningsmethode is in zekere mate verwant aan de klassieke wijze van r-waarden bepaling, met dien verstande dat voor ieder kinetisch experiment afzonderlijk curven in het $r_e - r_v$ vlak worden verkregen. De bepaling van de best passende r-waarden volgens deze methode blijkt een in geringe mate subjectieve werkwijze te zijn.

De tweede berekeningsmethode verschaft de mogelijkheid tot berekening van de r-waarden uit de gecombineerde gegevens van alle experimenten tegelijk. Het belangrijkste voordeel van deze procedure is dat, voor een bepaalde verzameling van experimentele gegevens, een éénduidig paar r-waarden verkregen wordt. Onder bepaalde beperkingen maakt deze methode het mogelijk de fout in de resulterende r-waarden te berekenen in termen van de betrouwbaarheidsintervallen.

Aangetoond wordt dat de experimentele gegevens verenigbaar zijn met het Alfrey model; de r-waarden zijn nauwkeurig bepaald. Voor de radicaal copolymerisatie van etheen en vinylacetaat in oplossing (*tert*-butanol) bij 62°C en 35 kg/cm^2 is

$$r_e = 0.743 \pm 0.010$$

en

$$r_v = 1.515 \pm 0.015 \; .$$

De implicaties van de resultaten worden besproken. Het blijkt dat de copolymerisatie van etheen en vinylacetaat onder de genoemde omstandigheden onverwacht goed door het Alfrey model wordt beschreven. De resulterende r_e-waarde vertoont een redelijke overeenkomst met enkele van de literatuurgegevens; de resulterende r_v-waarde echter is totaal verschillend van alle in de literatuur gevonden waarden. Deze discrepantie kan mogelijkerwijs verklaard worden door onopgemerkte inhomogeniteit van de reactiefase gedurende het hoge-drukproces dat gewoonlijk door andere onderzoekers wordt toegepast.

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LEVENSBERICHT

De schrijver van dit proefschrift werd op 1 februari 1939 geboren te Alphen aan den Rijn. Hij genoot zijn middelbare schoolopleiding aan het Rijks Lyceum te Steenwijk en behaalde het diploma HBS-B in 1957. In hetzelfde jaar begon hij zijn studie aan de Technische Hogeschool te Eindhoven in de afdeling der Scheikundige Technologie. Na een afstudeerperiode onder leiding van Prof. Dr. D. Heikens behaalde hij in 1964 het diploma van scheikundig ingenieur. Sinds zijn afstuderen is hij in dienst van de Technische Hogeschool te Eindhoven als wetenschappelijk medewerker bij de sectie Kunststoftechnologie van de groep Chemische Technologie.

STELLINGEN

1 De bewering van Hardy en Nyitrai dat de polymerisatiegraad van polyvinyleencarbonaat zou worden bepaald door overdrachtsreacties met het monomeer is ongegrond.

G. Hardy, K. Nyitrai, *Acta Chim. Acad. Sci. Hung.*, 56 (1968) 39.

2 Bij het opstellen van een kinetisch model waarin rekening wordt gehouden met anomale aanlegging tijdens de copolymerisatie van etheen met vinylacetaat en andere comonomeren, is door Lyubetzky c.s. ten onrechte aangenomen dat opeenvolgingen van twee of meer anomale aanleggingen geen rol spelen.

S. Lyubetzky, B. Erussalimsky, A. Goldenberg, *Dokl. Akad. Nauk SSSR*, 172 (1967) 1372.
S. Lyubetzky, A. Goldenberg, F. Duntoff, B. Erussalimsky, *J. Polymer Sci. C*, 6 (1968) 109.

3 De verklaring van Pogany voor de lagere γ-relaxatietemperatuur van fenolresolharsen ten opzichte van die van fenolnovolakharsen is zeer aanvechtbaar.

G.A. Pogany, *Polymer*, 10 (1970) 66.

4 De ontkleuring van plantaardige oliën met bleekaarde, in het algemeen toegeschreven aan verwijdering van de kleurstoffen door middel van fysische adsorptie, kan eveneens plaatsvinden door isomerisatie- en oxydatiereacties van de kleurstoffen.

H.P. Kaufmann, K.D. Mukherjee, *Fette, Seifen, Anstrichmittel*, 68 (1966) 896.
H. Hadorn, K. Zürcher, *Mitt. Lebensmitteluntersuchung und Hygiene*, 57 (1966) 189.

5 De reeds in een vroegtijdig ontwikkelingsstadium stormachtig toegenomen belangstelling voor de toepassing van gas-vloeistof chromatografie, heeft tot gevolg gehad dat de fysische achtergronden en de standaardisatie van deze scheidingsmethode onvoldoende aandacht hebben gekregen, waardoor haar wetenschappelijke ontwikkeling is vertraagd.

6 Bij de aanbeveling van de "Ricochet Trap" voor de beveiliging van vensterautoclaven, wordt ten onrechte geen aandacht besteed aan de invloed van de snelheidsverdeling van de bij desintegratie van een venster uitgestoten materie op de werking van deze beveiliging.

R.F. Recht, *Third International Conference on High Pressure*, Aviemore, May 11-15 (1970).

7 Gezien de betrouwbaarheid en de nauwkeurigheid van electronische drukopnemers is het weinig zinvol een drukbalans te ontwikkelen waarmee, door toepassing van electromagnetische evenwichtsinstelling, de waarde van de druk direct en continu afleesbaar is.

M. Bachelet, B. Vodar, *Third International Conference on High Pressure*, Aviemore, May 11-15 (1970).

8 Een regering die nalaat een jaarlijkse veiligheidskeuring voor auto's in te voeren alsmede ongedisciplineerd en agressief verkeersgedrag met kracht tegen te gaan, dient dan tenminste het bezit van motorrijtuigen in de Wapenwet te regelen.

Eindhoven, 1 december 1970 A.L. German