Monomer reactivity in free-radical copolymerization : high-pressure copolymerization as a tool in revealing structure-reactivity relations

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J. SCHRIJVER

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PROEFSCHRIFT

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Contents

Chapter 1

Introduction

1.1 Short historical survey

Scientific and industrial interest in the field of copolymerization dates back to the 1920's[1-3]. During the first decennia, the emphasis was mostly on the preparation and development of useful products. In the course of the numerous experiments to prepare various types of copolymers, it was frequently observed that the individual monomers were being built-in at different rates. As a result, copolymers of heterogeneous composition were obtained, often limiting their practical application as commercial products. Nowadays, a great number of copolymers are produced on a large industrial scale, and applied in an immense variety of products.

However, though copolymerization is most abundantly applied these days, monomer reactivity is still poorly understood. This observation concerns the main theme of the present investigation.

In the simultaneous polymerization of two vinyl monomers the more reactive monomer preferentially enters the polymer chain. As a consequence, determination of the composition of the copolymer formed yields information on the relative reactivity of the monomers.

The kinetic effect of high pressure is much greater than can be accounted for by the relatively minor increases in monomer concentration and are attributable to variations in the reaction rate constants caused by pressure. In the transition state theory the variation of the reaction rate constant with pressure is expressed by means of the activation volume $\Delta V^{\#}$. In this way, the magnitude of the pressure-effect is primarily a function of the difference in volume between the activated complex and the reactants, and through this of monomer structure.

The use of copolymerization and application of the concept of the activation volume is therefore obvious when studying structure-reactivity relations of monomers.

In 1944 Alfrey and Goldfinger[4], and Mayo and Lewis[5] independently derived the differential copolymer equation, that is found to hold for many free-radical copolymerizations. In principle, Young's compilation of copolymerization data should provide a rich source of information on reactivity in copolymerization, because the kinetic parameters of about 6000 copolymerizations have been tabulated[6]. However, the results appear to be contradictory and unsurveyable. There are two main reasons for this situation: the application of usually inaccurate experimental techniques and inadequate calculation procedures for the model parameters, i.e., the monomer reactivity ratios describing the copolymerization behavior of two monomers.

In 1971 German and Heikens[7] introduced a sequential sampling technique making the troublesome copolymer analysis superfluous. In this "sequential sampling" method the changing monomer feed composition is frequently analyzed throughout the copolymerization reaction by means of quantitative gas-liquid chromatography. Moreover, the data thus obtained can be directly used in the integrated form of the Alfrey-Mayo equation, which has many advantages (see subsequent paragraph and chapter 2). However, the application of this technique at high pressure still needed to be achieved. A new method of measuring monomer reactivity ratios under high-pressure conditions (up to 118 MPa (1 MPa = 10 bar) in the present investigation), which is based on the "sequential sampling" technique is described in chapter 5[8].

Reliable monomer reactivity ratios only can be obtained by applying nonlinear least squares to the integrated form of the Alfrey-Mayo copolymerization equation. Furthermore, it appeared imperative to take into account experimental errors in both measured variables (chapter 2). Although the Alfrey-Mayo model was published in 1944, it took till 1978 before van der Meer et al.[9] reported the improved curve-fitting I procedure, in which these conditions are fulfilled. Yamada et al.[10] and, more recently, Patino-Leal et al.[11] developed similar procedures. However, the application of all these calculation procedures requires the use of a high-speed computer. Therefore, research on simple linear methods still continues. In chapter 3 an easy and yet reliable calculation procedure[12] will be reported. Both the improved curve-fitting I and the newly developed linear regression procedure will be used in the present investigation.

From the above considerations it becomes clear, that only recently all conditions were being fulfilled to obtain reliable monomer reactivity ratios under a wide range of experimental conditions. In this stage, a thorough investigation of the factors governing reactivity of vinyl monomers in free-radical copolymerization and of relations between structure and reactivity in these monomers becomes possible and justified.

1.2 Scope of the present investigation

With respect to the relation between structure and reactivity of vinyl monomers the following general observations[1] served as a starting point:

(1) Monomers which possess bulky substituents may exhibit a certain reluctance to add to the corresponding macroradical, although frequently addition to other vinyl monomers, without hindering substituents may be possible.

(2) Another important factor is the extent of conjugation of the double bond with unsaturated groups in the substituents. This has been interpreted in terms of the amount of resonance stabilization of the macroradical produced by the reaction of the monomer with a growing radical chain end.

(3) A third factor is the electron density on the double bond affected by electron-withdrawing and electron-donating substituents.

The extent to which these factors affect reactivity and the relation with monomer structure is most effectively investigated by means of copolymerization of a series of monomers with a reference monomer. However, the copolymerization behavior of vinyl monomers does not only depend on the structure of the monomers, but also on the experimental conditions.

In (co)polymerization an effect of solvent on reactivity has to be expected in the case of polar monomers and monomers with functional groups capable of forming hydrogen bonds. The solvent-effect may also show up in the investigation of the effect of pressure on the reactivity of vinyl monomers. The observed pressure-effect does not only reflect the difference in volume between the transition and initial state due to bond formation and bond breaking, but also reflects the changing interaction between the reactants and the solvent molecules. In chapter 6 it will be shown that the simultaneous evaluation of the effect of both solvent and pressure enables a consistent interpretation of the relations between structure and reactivity in vinyl esters.

In the Alfrey-Mayo model four different propagation reactions are considered (Appendix). However, erroneous results are obtained if the relevant copolymerization cannot be described by this model and additional propagation reactions are playing a role. This may occur, for example, when depropagation reactions show up[13-15], penultimate groups affect reactivity[14-22], or a diene monomer is involved[22], showing up in different configurations in the copolymer chain. By means of an objective mathematical test[22] (see also chapter 2) it is concluded that the Alfrey-Mayo model is valid for the description of the kinetics of all copolymerizations reported in this thesis.

The information obtained by means of copolymerization is restricted to *pairs* of monomers. However, this hampers the correlation of reactivity with molecular structure of the individual monomers. Therefore several approaches have been developed to transpose the monomer reactivity ratios into parameters describing the reactivity of the individual monomers and radicals[23-30]. In addition, this would enable the prediction of the copolymerization behavior of monomers which have not yet been copolymerized. However, a detailed discussion of the various schemes is hampered by the fact that the monomer reactivity ratios found in the abundant literature fail to show mutual agreement, and it is difficult to find reliable data (chapter 2).

1.3 Aim and outline of the present investigation

The aim of the investigation described in this thesis is to gain more insight, both in a quantitative and qualitative way, in reactivity and relations between structure and reactivity of vinyl monomers and corresponding radicals by means of free-radical copolymerization.

Moreover, a detailed investigation of copolymerization kinetics implies that considerable attention has to be paid to the development of experimental methods and computational procedures, enabling a reliable determination of monomer reactivity ratios.

The conditions which have to be fulfilled to calculate reliable monomer reactivity ratios are discussed in chapter 2. Several approaches have been developed to describe the reactivity of the separate monomers. The most widely used scheme, viz., the *Q-e* scheme, is compared with the promising *Patterns of Reactivity* approach.

A new, very simple and yet reliable method for the calculation of monomer reactivity ratios, based on the observation of the linearity of the plot ln n_1 vs. ln n_2 is described in chapter 3.

Chapter 4 deals with the effect of pressure on (co)polymerization. The influence of solvent and steric hindrance on the activation volume is discussed. Major attention is paid to the prediction of the pressure-effect on the monomer reactivity ratios. Two existing hypotheses are compared with a new approach based on the Hammond postulate.

In chapter 5 a novel direct sampling of reaction mixtures under high-pressure conditions, followed by on-line gas chromatographic analysis of the sample, is described.

Vinyl monomers can be roughly divided into two classes: conjugated and unconjugated monomers.

In chapter 6 the relations between structure and reactivity of a homologous series of vinyl esters (unconjugated monomers) are described. Newly proposed views are applied to earlier and new results.

The copolymerizations of a number of conjugated monomers with styrene as reference monomer are described in chapter 7, with emphasis on the effect of pressure on the reactivities of these monomers. The results are compared with those obtained in the investigation of the vinyl esters.

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Chapter 2

Fundamental Aspects of Free-Radical Copolymerization

Synopsis

The investigation of relations between structure and reactivity of vinyl monomers by means of copolymerization requires an exact description of copolymerization kinetics. The model most frequently used is the Alfrey-Mayo equation. The conditions which have to be fulfilled in order to calculate reliable model parameters, i.e., the r *values are discussed. The information obtained by means of copolymerization is restricted to* pairs *of monomers. Several approaches have been developed to transpose the* r *values into parameters describing the reactivity of the separate monomers. A reliable model description should avoid arbitrary assignment of model parameters. Furthermore, an appropriate scheme should take into account contributions which depend on the structure of* both *monomer and corresponding radical. These conditions will be illustrated by the comparison between the most widely used scheme, viz., the* Q-e *scheme and the "Patterns of Reactivity" approach. In our opinion the latter is at present the most reliable scheme for describing reactions between polymer radicals and monomers.*

2.1 Introduction

The model most frequently used for the description of copolymerization kinetics is the Alfrey-Mayo (AM) model[1,2]. Investigation of structure-reactivity relations of vinyl monomers by means of copolymerization is entirely based on the knowledge of the pertaining model parameters, viz., the monomer reactivity ratios. Therefore, an exact and reliable method for the evaluation of these r values is a necessity. However, it appears that there is no unique calculation procedure. Reliable r values only can be obtained by applying nonlinear least squares to the integrated copolymer equation[2,3]. Furthermore, it is necessary to take into account experimental errors in all measured variables. These conditions are only fulfilled in three recent calculation procedures[4,5,6]. Most other existing procedures can be found in three reviews[4,7,8]. The reasons underlying the development of a great number of unreliable calculation procedures will be discussed.

The information obtained by means of copolymerization is restricted to pairs of monomers. Therefore, many investigators have attempted to transpose the r values into parameters describing the relations between structure and reactivity of individual monomers[9-16]. In addition it should be possible to predict the r values of monomer pairs which have not yet been copolymerized. However, for a number of reasons several methods inherently fail to give a reliable description of monomer reactivity. In the first place it is believed that the reactivity of a monomer strongly depends on the nature of the attacking radical. Therefore, a theoretical treatment of reactivity should include contributions which depend on the structure of *both* radical and monomer. Secondly, the application may be restricted to certain classes of monomers. Also the "standard" monomers may be too similar in character. Finally, most methods require arbitrary attribution of reference parameters and basically differ only in whether one chooses to work in terms of two, three or four parameters. The codification of r values will be illustrated by the comparison between the most widely used scheme, i.e., the *Q-e* scheme[9] and the "Patterns of Reactivity" approach[11], referred to as *Patterns*, which at present is thought to be the most reliable scheme.

2.2 Copolymerization kinetics

According to Alfrey and Mayo[1,2], under a number of conditions, only four chain propagation reactions have to be considered for the description of the simultaneous free-radical polymerization of two vinyl monomers.

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1\cdot$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_1\cdot$$

Combining the equations for monomer consumption and the steady-state principle the following equation can be derived (Appendix):

$$\frac{dn_1}{dn_2} = \frac{r_1 q + 1}{r_2/q + 1} \tag{2.1}$$

where, dn_1/dn_2 is the ratio of the instantaneous rates of consumption of the monomers by chain propagation; $q = n_1/n_2$ is the ratio of the number of moles of monomer M_1 and M_2 respectively; $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the monomer reactivity ratios or r values expressing the preference of a given radical chain for the corresponding monomer over the other. In other words, the r values are reflecting the *relative* reactivity of two monomers towards a radical chain end. Eq. 2.1 is called the Alfrey-Mayo (AM) model. In case the copolymerization cannot be described by the AM model (see chapter 1) more than four chain propagation reactions have to be considered, leading to extended schemes with more than two kinetic parameters.

2.3 Evaluation of the monomer reactivity ratios

According to eq. 2.1 the r values of a monomer pair can be determined by means of compositional analysis of copolymer formed for a number of initial monomer feed ratios. The experimental technique used is based on the isolation, purification and analysis of the copolymer. However, for a number of reasons this method does not yield reliable r values. The most important drawback is the fact that most copolymerizations inevitably will show a drift in monomer feed ratio *q*, due to the different reactivity of the monomers, as the degree of conversion increases and, consequently, so does the composition of the formed copolymer. In addition it is questionable which value for *q* has to be used in eq. 2.1. Some improvement can be obtained in using the mean value of the initial and final monomer feed ratios. As a consequence, to limit the drift in *q*, the conversion to copolymer has to be kept as small as possible. However, we have shown quantitatively that this may lead to erroneous results when conversion of one of the monomers is within experimental error[17]. Furthermore, it should be emphasized that nonstationary reaction conditions occurring at the start of copolymerization demand high-conversion experiments. A further drawback is that sometimes even within one binary combination different analytical techniques are needed. As a consequence, the experimental errors are unknown because different techniques invariably lead to different results for the same sample.

The evaluation of *r* values with eq. 2.1 essentially is a nonlinear least squares (NLLS) problem which has to be solved with the aid of a computer. However, computers only became available since about 1965, whereas the AM model was published in 1944. Investigators, aiming at linearization of eq. 2.1, tackled this problem in various ways, leading to a great number of calculation procedures. Transformation of the AM equation leads to transformation(s) of the original error structure of the measured variables. The transformed error no longer has an expected value of zero so that essential information will have been lost and only approximate *r* values will be found. Our views in this matter were confirmed recently by McFarlane et al.[18] who compared six linear regression methods with a NLLS method by means of simulated copolymerization experiments. For chosen *r* values the copolymer composition was computed from eq. 2.1 for a number of monomer feed ratios. To each of the computed values was added a normally distributed, random error with mean zero and known variance. The resulting data were then analyzed with the various methods. The resulting *r* values were compared with the initial values, resulting in the rejection of three methods. However, this way of comparison at *zero* conversion is meaningless. The main problem in copolymerization kinetics is the continuous change in monomer feed composition as the degree of conversion increases. For this reason even the NLLS procedure may go wrong, although the degree of bias naturally depends on the monomer reactivity ratios and the values of q.

From the above considerations it becomes clear that the vast number of r values, as e.g. tabulated in the Polymer Handbook[19], may be much more biased by the unreliable methods of calculating them from the copolymerization experiments than by the differences in experimental conditions. For example, Percec et al.[20] reexamined 25 free-radical copolymerizations using the (linear) Kelen and Tüdős method[21]. Of these, only 12 could be characterized by the underlying AM model. Five systems presented high scattering of experimental data given by the original authors; 2 systems belong to another copolymerization scheme, and 6 gave meaningless r values. Therefore, the foregoing should serve as a warning against casual acceptance of single numbers.

To obtain reliable r values two basic improvements are necessary[4]:

- replacement of the compositional analysis of initial feed and copolymer formed, by monomer feed compositional analysis;
- an exact relationship describing copolymerization kinetics up to high conversions.

The first improvement became possible by the introduction of gas-liquid chromatographic (GLC) analysis[22,23] and avoids the drawbacks of the conventional method. Moreover, there are some additional advantages:

(1) gaseous monomers can be used more easily;

(2) samples can be taken throughout the copolymerization reaction (sequential sampling technique)[22].

Integration of eq. 2.1 yields an exact relationship between the changing monomer feed ratio (q) and the degree of conversion, based on M_2 (f_2) (Appendix):

$$f_2 = 100\cdot\left[1 - \left(\frac{q}{q_o}\right)^{-x_2-1}\left(\frac{x_2 q - x_1}{x_2 q_o - x_1}\right)^{x_1+x_2+1}\right] \qquad (2.2)$$

where, $f_2 = 100\cdot\left(1 - \frac{n_2}{n_{20}}\right)\%$, degree of conversion of M_2; $x_1 = 1/(r_1 - 1)$ and $x_2 = 1/(r_2 - 1)$.

The subscript zero indicates conditions at zero conversion. Eq. 2.2, which is called the integrated AM equation can be used up to relatively high conversions (20-40%).

At first glance, the use of GLC analysis in combination with a NLLS procedure, based on the integrated AM model, should yield reliable r values. However, an important condition for application of least squares procedures, viz., the experimental error in the independent variable is zero or small as compared to the experimental error in the dependent variable, is not fulfilled. By using GLC the errors in both variables q and f_2 are in the same order of magnitude. As a consequence, both q and f_2 can be used as dependent variable, resulting in different values for the monomer reactivity ratios. These views have recently been confirmed by Patino-Leal et al.[6]. They compared their EVM procedure that takes into account experimental errors in both $[M_1]$ and $[M_2]$ with a NLLS procedure that only considers measurement errors in one of the variables. The results are given in Table 2-1.

Table 2-1 Results from simulated copolymerization experiments for $r_1 = 0.1$ and $r_2 = 10$[a], according to Patino-Leal et al.[6].

Method	$\bar{r}_1$	$\bar{r}_2$	RMSD ($\hat{r}_1$)	RMSD ($\hat{r}_2$)
EVM	0.1016	10.0827	0.0082	0.5826
LS-a	0.1031	10.1949	0.0124	0.7778
LS-b	0.0281	6.0872	0.0733	4.2596

[a] LS-a refers to the use of NLLS with $[M_1]$ as dependent variable, and LS-b assumes $[M_2]$ as the dependent variable; RMSD is the root-mean-square deviation.

Therefore, the use of a calculation procedure, based on the integrated AM equation, that considers experimental errors in all measured variables, is a basic improvement in the science of the determination of r values[4,5,6]. In this thesis a procedure recently developed in our laboratory, i.e. the improved curve-fitting I procedure[4], in combination with GLC analysis of the reaction mixture will be used. This estimation procedure is believed to be at present the most accurate one for computing r values.

However, for reasons of simplicity linear methods continue to be popular among copolymerization workers. To meet this desire, we developed an easy and still reliable calculation procedure, based on the linearity of the plot ln n_1 vs. ln n_2 (chapter 3 and ref. 17). The range of validity of this method is determined by comparison with the improved curve-fitting I procedure[4] by means of simulated copolymerization experiments. The method, given the experimental setup and the error structure described, appears to be applicable to a wide range of values of $r_1 \cdot r_2$, that is, when $0.001 < r_1 \cdot r_2 < 2$, provided both M_1 and M_2 conversions are large enough compared with the measurement error.

In a number of cases (see chapter 1) the AM model cannot describe the observed copolymerization behaviour. Kelen and Tüdős[24,25] have applied their linear procedure as a model-discriminating tool. It was assumed that a system requiring more than two kinetic parameters to describe it, would exhibit a systematic departure from linearity in the plot of the dependent variable η vs. the independent variable ξ. While this is correct, McFarlane et al.[26] stated and confirmed that the nature of the Kelen-Tüdős plot and the error structure can also cause a systematic deviation from the rectilinear plot. Therefore, it was concluded that a linear least-squares analysis of copolymer composition data cannot serve, by itself, as a model discriminating system. Van der Meer et al.[27] outlined two methods to detect possible deviations from the AM model. The first method is based on examining the various lines in a r_1 vs. r_2 plot, obtained by means of the improved curve-fitting I/*intersection* procedure[4]. The slope of these lines depends mainly on the average monomer feed composition. If there is a drift of the intersection points as a function of the monomer feed composition the AM model has to be rejected. In the second and more objective method, viz., the F test, based on the statistical comparison of residual sums of squares, it is possible to check the goodness of fit of any copolymerization scheme. Furthermore, the test allows one to decide which of two alternative schemes is preferred for a given copolymerization reaction. It is very important to be able to detect possible deviations from the AM model, but, it is even more important to assess the appropriate scheme. Therefore, the F test is preferred in selecting the most probable kinetic scheme for a given copolymerization system.

2.4 Inherent reactivity of monomers and radicals

2.4.1 Introduction

There are two main reasons why considerable importance has been attached to the development of schemes in which each individual monomer is described by characteristic constants. In the first place, the need to determine r values for all possible pairs among a large number of monomers can be avoided. Secondly, if each monomer, rather than each pair of monomers, can be characterized by a set of numerical constants, the correlation of reactivity with molecular structure becomes more attainable than if one must consider the structure of two monomers together. Once, the model parameters for a given scheme have been assigned, it becomes possible to predict r values for pairs of monomers for which the model parameters are known, but which have not yet been copolymerized. A number of factors governing the reactivity of a vinyl monomer will be discussed in the subsequent section.

First, there is evidence for a *steric* effect. Monomers which possess substituents on both carbon atoms of the double bond (1,2-disubstituted ethylenes) exhibit, in general, a reluctance to homopolymerize. However, very often copolymerization with other vinyl monomers, without hindering substituents, is possible. A second important factor seems to be the extent of conjugation of the double bond with unsaturated groups in the substituent. In other words, this represents the amount of *resonance* stabilization of the radical adduct produced by the reaction of the monomer with a growing chain end. Thus, styrene is a very reactive monomer, whereas the styrene radical is a fairly unreactive radical due to the large gain in resonance stabilization. The reverse applies to vinyl acetate. These effects tend to counteract each other[28]: the self-growth of styrene (unreactive radical plus reactive monomer) may be quite comparable in rate with the self-growth of vinyl acetate (reactive radical plus unreactive monomer). However, when styrene and vinyl acetate must compete for a given free radical, as is the case in copolymerization, the greater reactivity of the styrene monomer becomes very evident. Therefore, the separate polymerization behavior of individual monomers is a poor guide for the prediction of their copolymerization behavior.

The foregoing may lead to the conclusion that the order of reactivity for radicals is approximately the reverse of that for monomers. However, the validity of an absolute order of reactivities of radicals and monomers is vitiated by a third factor: the *polarity* of the carbon-carbon double bond. In case of radicals with intermediate reactivity the polar effect can bring about a striking change in the reactivity sequence. Substituents able to withdraw or donate electrons affect the polarity of monomers and radicals. A free radical with a positive character will exhibit a particular preference for a monomer with an electron rich double bond and vice versa.

A great number of schemes have been developed which aim to correlate structure and reactivity of vinyl monomers with the three factors discussed above. Several of these originate from organic chemistry. Typical examples are the Yamamoto-Otsu equation[13], the Hammett equation[14], and the Taft relation[15]. In these schemes the monomer reactivity of a homologous series of monomers towards a reference radical is considered. Basically related to this type of approach are semi-empirical schemes based on the derivation of an expression for the rate constant pertaining to the reaction of a radical with a monomer[9,10,11,29]. The r values, as defined, then can be predicted by calculating the ratio of the rate constants for the reaction of a radical with the corresponding monomer and with the comonomer. In addition, there are several theoretical approaches based on absolute calculations of "electron densities" or some related property, assumed to determine reactivity. A number of authors have attempted to give a theoretical basis to existing schemes, e.g., the *Q-e* scheme[29-32].

The validity of the various schemes can be determined by the comparison of the predicted r values with those experimentally obtained. However, as already pointed out in section 2.3, the r values found in the abundant literature fail to show mutual agreement and it is difficult to find reliable ones. As a consequence, it is impossible to decide the extent to which the separate schemes are valid or to find out which one has the best descriptive character. For the same reason the existing schemes will not be reviewed thoroughly in this chapter. The discussion will be restricted to the conditions that have to be satisfied in order to provide a reliable description of structure-reactivity relations and a reliable prediction of r values. This will be achieved by the comparison of the most widely used scheme, viz., the *Q-e* scheme[9] and the *Patterns* method[11], which at present we consider to be the most reliable scheme. Detailed discussion of these and other schemes can be found in the references mentioned before.

2.4.2 *Q-e* scheme

The underlying assumption of the *Q-e* scheme is that the rate constant k_{12} for the reaction of radical $\sim M_1\cdot$ with monomer M_2 is given by the following relationship:

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \qquad (2.3)$$

where P_1 is a constant characteristic of the nature of the radical, Q_2 is the general reactivity in terms of stabilization by resonance of the monomer, and e_1 and e_2 are the polarities of radical and monomer, respectively. Assuming the same polarity factor e for monomer and corresponding radical, the r values may be expressed as follows:

$$r_1 = k_{11}/k_{12} = Q_1/Q_2 \exp[-e_1(e_1-e_2)] \qquad (2.4)$$

$$r_2 = k_{22}/k_{21} = Q_2/Q_1 \exp[-e_2(e_2-e_1)] \qquad (2.5)$$

and

$$r_1 \cdot r_2 = \pi = \exp[-(e_1-e_2)^2] \qquad (2.6)$$

Monomer reactivity ratios furnish values for ratios of Q factors and differences between e factors. Therefore, a zero point has to be chosen by assigning arbitrarily Q and e parameters for one monomer. At present styrene is used as reference monomer with $Q = 1.0$ and $e = -0.8$. Once *Q-e* values have been assigned it becomes possible to predict reactivity ratios for pairs of monomers for which *Q-e* values are known but which have not actually been copolymerized; the potential value of the *Q-e* scheme is therefore obvious.

2.4.3 *Patterns*

The *Patterns* method is a more general one compared with the *Q-e* scheme as the reaction between any radical and any monomer is considered. The authors claim that the reaction rate constant in question can be expressed as:

$$\log k = \log k_{3,\mathrm{T}} + \alpha\sigma + \beta \tag{2.7}$$

where $k_{3,\mathrm{T}}$ is the measured rate constant for a specific reaction, i.e., the hydrogen abstraction by the radical $R\cdot$ from toluene. Of the other parameters the Hammett σ function represents the polarity of the radical $R\cdot$, and α and β are characteristic of the substrate, experimentally determined by reaction of the substrate with a series of reference radicals of known $k_{3,\mathrm{T}}$ and σ. As a consequence, *Patterns* avoids any arbitrary assignment of reference values. In case of a transfer reaction the first and third terms of the right hand side of eq. 2.7 depend upon the dissociation energies of the bonds broken and formed. The term β is also a measure of the polarity of the transition state in case of a radical with only nonpolar substituents ($\sigma = 0$). The second term on the right hand side measures the additional polar effect which appears if the radical is substituted with polar groups. The term $\alpha\sigma$ denotes both the magnitude of the contribution of polar structures to the transition state and the direction of charge transfer between radical and monomer. Negative values of α correspond to a tendency to transfer an electron from the radical to the substrate, while positive values are associated with partial proton transfer from substrate to radical.

In copolymerization the r values can be predicted by the following equations:

$$\log r_1 = \sigma_1 \cdot (\alpha_1 - \alpha_2) + (\beta_1 - \beta_2) \tag{2.8}$$

$$\log r_2 = \sigma_2 \cdot (\alpha_2 - \alpha_1) + (\beta_2 - \beta_1) \tag{2.9}$$

2.4.4 Comparison between *Q-e* scheme and *Patterns*

An obvious limitation of the *Q-e* scheme is the need to assign arbitrary Q and e parameters to a reference monomer. At present styrene is used with $Q = 1.0$ and $e = -0.8$, although there have been several attempts to change the latter[9,33,34] or to take ethylene as a more logical reference monomer[28,35,36], in order to obtain a better physical significance of the parameters. However, the original *Q-e* scheme has become so firmly entrenched that it does not seem possible either to modify or to replace it. The most important drawback of the *Q-e* scheme is the assignment of similar polarity values to radical and monomer. Therefore, as can be seen from eqs. 2.4 and 2.5 the prediction of r values is governed by monomer parameters, independent of the nature of the radicals. However, in our opinion the experimentally observed difference in reactivity of two monomers, as expressed in the r values, strongly depends on the reactivity of the attacking radical. For example, Jenkins[30] provides relative rate constants for propagation and transfer reactions of three radicals towards five substrates. The ratio between reactivities of vinyl acetate and acrylonitrile radicals towards the substrates varies from 10^4 to 5, whereas the ratio between reactivities for styrene and acrylonitrile radicals changes from 10^2 to 2.10^4. Additional proof is found in our investigation of the effect of pressure on the copolymerization of a homologous series of vinyl esters with ethylene as reference monomer (see chapter 6). The results suggest the conclusion that the greater the radical reactivity, the smaller the difference in monomer reactivity experimentally observed. As a consequence, there is no doubt that the order of reactivities of radicals is not unique, but depends on the nature of the particular radical-substrate combination. Therefore, an appropriate scheme relating structure to reactivity and predicting r values should have at least one parameter describing the reactivity of the radical. Wall[10] has suggested that improved fit with experimental data can be obtained if the *Q-e* scheme is expanded by assigning a different e value to a monomer and the corresponding radical (e^*). Wall's expressions are:

$$r_1 = Q_1/Q_2 \exp[-e_1^*(e_1-e_2)] \qquad (2.10)$$

$$r_2 = Q_2/Q_1 \exp[-e_2^*(e_2-e_1)] \qquad (2.11)$$

$$r_1 \cdot r_2 = \pi = \exp[-(e_1-e_2)(e_1^*-e_2^*)] \qquad (2.12)$$

This extension does involve the need for the arbitrary assignment of an additional parameter, i.e. an e^* reference value and tends to undermine the utility of the modification. The same holds for other methods that require arbitrary attribution of values to standard parameters and basically only differ in whether one chooses to work in terms of two, three or four parameters. Although *Patterns* is a four parameter scheme it has the advantage that all these parameters are experimentally accessible. Therefore, deviations between the predicted and observed r values, provided the latter are determined reliably, originate from the differences in experimental conditions and the reliability with which the parameters are determined. An additional advantage of *Patterns* is the treatment of propagation and **transfer** reactions with equal facility, whereas other methods except one[37], exclusively deal with propagation reactions.

The difference between the *Q-e* scheme and *Patterns* is most elegantly shown by consideration of a system of three monomers A, B and C which are copolymerized in pairs to give a total of six reactivity ratios[30,31]. Mayo[38] defined the function H such that

$$H = \frac{r_{AB} \cdot r_{BC} \cdot r_{CA}}{r_{AC} \cdot r_{CB} \cdot r_{BA}} \qquad (2.13)$$

By substitution of the expressions for the r values from the *Q-e* scheme (eqs. 2.4 and 2.5) it is evident that the only possible value for H is unity. With *Patterns* the following result is obtained:

$$-\log H = \sigma_A \cdot (\alpha_B-\alpha_C) + \sigma_B \cdot (\alpha_C-\alpha_A) + \sigma_C \cdot (\alpha_A-\alpha_B) \qquad (2.14)$$

As a consequence, H can be calculated a priori from the known σ and α values for the three monomers and the derived radicals. The calculated H then can be compared with the H obtained by substitution of the experimental values of the six monomer reactivity ratios

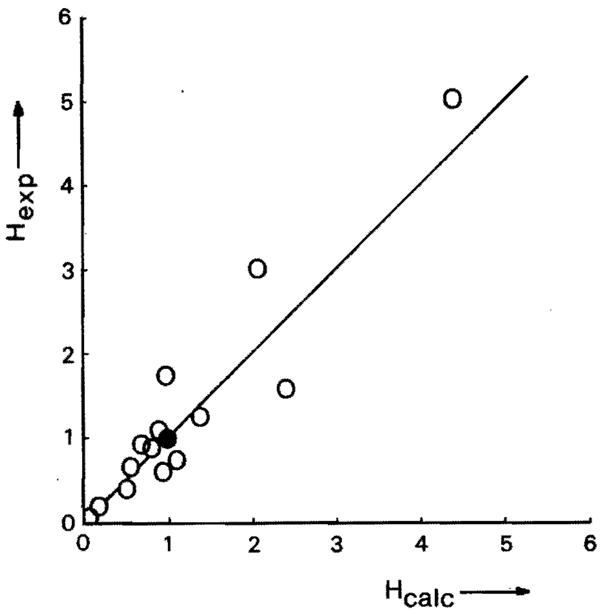

Figure 2-1 Comparison between observed *H* factors and those calculated by means of the *Patterns* treatment[31].

in eq. 2.13. Figure 2-1 displays the comparison for fourteen systems, each comprising three monomers (according to Jenkins[31]). It is apparent that *H* does depart significantly from unity. In chapter 7 we will also show that *H* is unity is an unrealistic assumption, not confirmed by experimental data. Furthermore, the observed values correlate well with those calculated. This is a clear demonstration of the power of the *Patterns* treatment where the *Q-e* scheme fails completely to cope with the situation.

2.4.5 Conclusions

A theoretical treatment of reactivity should include contributions which depend on the structures of *both* radical and monomer. On this view the frequently used *Q-e* scheme is inappropriate to relate structure and reactivity and to predict *r* values since only monomer parameters are considered. Therefore, attempts to support the *Q-e* scheme with quantum chemical studies are useless. However, attaching real significance to the *Q-e* parameters was not the object of the originators of the scheme. "The most that can be claimed is that to a reasonable approximation the *Q-e* scheme permits the codification of copolymerization results in terms of *Q* and *e* values of the various monomers"[28]. Therefore, the assignment of *Q* and *e* values is quite empirical being derived from copolymerization data in such a way that a self-consistent set of parameters is obtained. In this view the *Q-e* scheme still can be used for an approximate prediction of *r* values of uninvestigated combinations while it is remembered that the scheme possesses only a limited theoretical foundation. The distinction between *Q-e* scheme and *Patterns* lies in different allocation of separate polar parameters to monomers and the corresponding radicals. *Patterns* therefore represents an advance on *Q-e* in the same sense as *Q-e-e** but with the invaluable advantage that its basis consists of experimentally determined reference data, devoid of arbitrary assignment.

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Chapter 3

A New Method of Estimating Monomer Reactivity Ratios in Copolymerization by Linear Regression

Synopsis

Sequential gas-liquid chromatographic analysis of the reaction mixture throughout a copolymerization reaction in conjunction with the improved curve-fitting I (integrated form) method, which accounts for measurement errors in both variables, allows accurate estimation of the monomer reactivity ratios. In this chapter an alternative method is presented for estimating r *values in copolymerization with linear regression only, which is especially suited to cases in which one or two of the* r *values is close to 1. In these cases the improved curve-fitting I method tends to converge slowly because of the numerical instability of the integrated copolymerization equation. The use of the new method is illustrated for the estimation of the* r *values for ethylene and vinyl acetate in benzene at 3.4 MPa and 335 K. The linear regression method was also tried on other copolymerizations and the results are compared with those obtained from the improved curve-fitting I method. The limits of applicability of the linear regression method are determined by simulated "sequential sampling" experiments. It appears that the new method is applicable when the product of the* r *values is between 0.001 and 2, provided both monomer conversions are large enough compared with the measurement error.*

3.1 Introduction

This chapter is intended to describe an easy-to-use monomer reactivity ratios estimation method. For a review of other existing methods see Tidwell and Mortimer[1], Joshi[2], and van der Meer et al.[3].

Gas-liquid chromatographic (GLC) analysis allows accurate determination of monomer feed composition throughout a copolymerization reaction up to relatively high conversions (20-40%)[4,5]. By integrating the simple copolymer equation of Alfrey and Mayo[6,7]

$$\frac{dn_1}{dn_2} = \frac{r_1(n_1/n_2) + 1}{r_2(n_2/n_1) + 1} \tag{3.1}$$

where n_1 and n_2 are the number of moles of monomer M_1 and M_2, respectively, and r_1 and r_2 are the monomer reactivity ratios, we can express n_2 as a function of the monomer feed ratio $q = n_1/n_2$:

$$\frac{n_2}{n_{20}} = \left(\frac{q}{q_0}\right)^{-x_2-1} \left(\frac{x_2 q - x_1}{x_2 q_0 - x_1}\right)^{x_1+x_2+1} \tag{3.2}$$

where n_{20} and $q_0 = n_{10}/n_{20}$ represent the initial conditions and $x_1 = 1/(r_1 - 1)$ and $x_2 = 1/(r_2 - 1)$.

Sequential GLC analysis yields observations N_{2i} for n_{2i} and Q_i for q_i (i = 1,...,n) during a number of experimental runs. The observations are assumed to be without systematic error and have variances equal to $\sigma^2(N_{2i})$ and $\sigma^2(Q_i)$, respectively, with correlation effect ρ_i. We further assume that (N_{2i},Q_i) is independent of (N_{2j},Q_j) for $i \neq j$. Estimates for the values of $\sigma^2(N_{2i})$, $\sigma^2(Q_i)$, and ρ_i are obtained by consideration of the relationship between the errors in N_{2i} and Q_i and the errors in the three peak areas A_{1i}, A_{2i} and A_{si} occuring in the sequential gas chromatographic analysis of the copolymerization mixture[3]. For simplicity we assume that the variances are equal to 1 and that the correlation coefficient is zero.

The parameters r_1 and r_2 are estimated by solving

$$\min_{\substack{R,Q_j \\ j=1,\ldots,n}} \sum_{i=1}^{n} \left[(N_{2i} - n_{2i})^2 + (Q_i - q_i)^2\right] \tag{3.3}$$

subject to eq. (3.2), where R constitutes r_1 and r_2 and the initial monomer feed ratios for each experimental run. A justification for this criterion can be found in van der Meer et al.[3] together with an approximate expression for the covariances of the parameter estimates and a description of the improved curve-fitting I method for general values of $\sigma^2(N_{2i})$, $\sigma^2(Q_i)$, and ρ_i. This method is also applicable for more complicated copolymerization models[8]. An efficient algorithm for solving eq. (3.3) has been described by Linssen[9,10].

In this chapter we present an alternative method of estimating r_1 and r_2, which requires only linear regressions, and we compare the results of the two methods for a number of cases.

3.2 Estimating r_1 and r_2 with linear regression

3.2.1 The general behavior of the solution to the copolymer equation

The solution (3.2) to the copolymer equation (3.1) may be written directly in terms of the number of moles n_1 and n_2 as

$$r_1(1 - r_2)\ln n_2 + r_2(1 - r_1)\ln n_1 - (1 - r_1r_2)\ln\left|\left(n_1 + \frac{1 - r_2}{r_1 - 1}n_2\right)\right| = C_0 \tag{3.4}$$

where

$$C_0 = (1 - r_2)(r_1 - 1)\ln n_{20} + r_2(1 - r_1)\ln q_0 - (1 - r_1r_2)\ln\left|\left(q_0 + \frac{1 - r_2}{r_1 - 1}\right)\right| \tag{3.5}$$

and $q_0 = n_{10}/n_{20}$. Figure 3-1 shows a plot of ln n_1 vs. ln n_2 for $r_1 = 0.74$, $r_2 = 1.5$ (I); $r_1 = 10$, $r_2 = 0.1$ (II); and $r_1 = 0.5$, $r_2 = 10$ (III), and initial conditions $n_{20} = n_{10} = 1$. It is seen from this plot that the relation between ln n_1 and ln n_2 is smooth and (provided $r_1 \cdot r_2 \sim 1$) even for extremely large variations in q (say $q_{max}/q_{min} = 10{,}000$) the slope of the curve hardly changes at all. Therefore for small ranges of q_{max}/q_{min} we have, to an excellent approximation,

$$d \ln n_1/d \ln n_2 = \beta$$

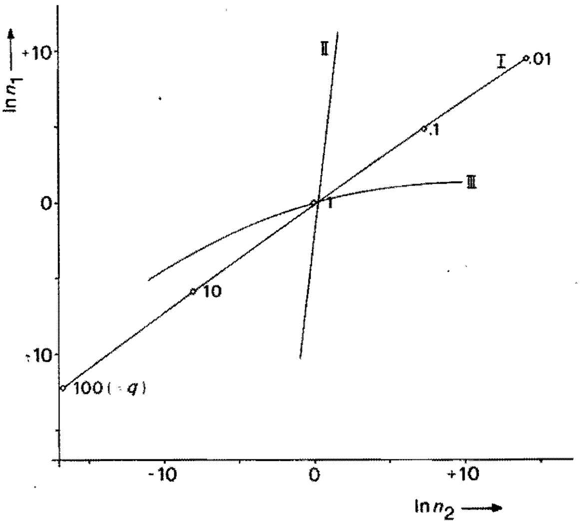

Figure 3-1 $\ln n_1$ vs. $\ln n_2$ for $r_1 = 0.74$, $r_2 = 1.5$ (I); $r_1 = 10$, $r_2 = 0.1$ (II); and $r_1 = 0.5$, $r_2 = 10$ (III); and corresponding values of q for case I; $n_{10} = n_{20} = 1$.

Now the Alfrey and Mayo equation (3.1) can be written

$$\frac{d \ln n_1}{d \ln n_2} = \frac{r_1 q + 1}{r_2 + q}$$

Consequently we have

$$\beta = \frac{r_1 \overline{q} + 1}{r_2 + \overline{q}} \tag{3.6}$$

where $\overline{q}$ is some intermediate value between $q_{\min}$ and $q_{\max}$. The extreme slopes are $\beta = r_1$ as $q \to \infty$ and $\beta = 1/r_2$ as $q \to 0$ so the difference in slopes is very small (in example I the change is only 0.0733). Different initial conditions result in simply translated lines in the $\ln n_1$-$\ln n_2$ plane.

3.2.2 The linear regression estimation procedure

From the preceding section we see that the problem of fitting curves of form (3.4) to several sets of data is equivalent to fitting small segments of smooth curves. For limiting excursions of q the relation between $\ln n_1$ and $\ln n_2$ is essentially linear. It is therefore reasonable to estimate r_1 and r_2 by using the following steps:

(1) For the jth experimental run, $j = 1,2,\ldots,N$, convert the area readings to relative number of moles and the ratio of the number of moles of monomer M_1 and M_2

$$y_{ji} = \ln \frac{A_{1ji}}{A_{sji}}, \quad x_{ji} = \ln \frac{A_{2ji}}{A_{sji}}, \quad Q_{ji} = \frac{A_{1ji}}{A_{2ji}} \cdot C_j$$

where y relates to monomer 1, x to monomer 2, C_j is a known system constant, and $i = 1,\ldots,n_j$.

(2) Calculate $\overline{Q}_j = (1/n_j) \sum_{i=1}^{n_j} Q_{ji}$

(3) Fit a linear model

$$y_{ji} = \alpha_j + \beta_j x_{ji}, \quad i = 1,2,\ldots,n_j$$

using simple linear least squares to obtain an estimate $\hat{\beta}_j$. Because there are errors in x and y, we also fit the model

$$x_{ji} = \gamma_j + \delta_j y_{ji}, \quad i = 1,2,\ldots,n_j$$

and take as the estimate of the slope

$$\tilde{\beta}_j = (\hat{\beta}_j/\hat{\delta}_j)^{1/2}$$

(4) Use the estimates $(\tilde{\beta}_j, \overline{Q}_j)$ as data to fit the model

$$\tilde{\beta}_j = \frac{\overline{Q}_j r_1 + 1}{r_2 + \overline{Q}_j}, \quad j = 1,2,\ldots,N \tag{3.7}$$

hence obtain the estimates $\hat{r}_1, \hat{r}_2$.

Note that it is not necessary to use nonlinear least squares to estimate r_1 and r_2, because a simple grid search on r_2 can be used to advantage. We note that for a given value of r_2, say r_{2k}, eq. (3.7) reduces to a linear model in r_1; that is

$$\tilde{\beta}_j - \frac{1}{r_{2k} + \bar{q}_j} = r_1 \left(\frac{\bar{q}_j}{r_{2k} + \bar{q}_j} \right)$$

Letting

$$u_j^k = \tilde{\beta}_j - \left(\frac{1}{r_{2k} + \bar{q}_j} \right), \quad v_j^k = \left(\frac{\bar{q}_j}{r_{2k} + \bar{q}_j} \right)$$

we have

$$u_j^k = r_1 v_j^k$$

hence the conditional least-squares estimate for r_1 is

$$\hat{r}_{1k} = \hat{r}_{1k}(r_{2k}) = \Sigma\, u_j^k v_j^k / \Sigma\, (v_j^k)^2 \tag{3.8}$$

with residual sum of squares $S_k = \Sigma\, (u_j^k)^2 - \hat{r}_{1k}^2 \cdot \Sigma\, (v_j^k)^2$. It is a simple matter to step through a range of values of r_2, say r_2 [1.05 (0.05) 2.00], calculate $\hat{r}_{1k}$ and S_k at each value, and then choose the pair $[\hat{r}_1(\hat{r}_2), \hat{r}_2]$ that gives the smallest residual sum of squares, which we call S. Note also that step (4) depends on which monomer is subscripted with 1. If we change the subscripts, step (4), that is, regression of $\tilde{\beta}$ on $\bar{q}$, is replaced by the regression of $1/\tilde{\beta}$ on $\overline{1/q}$. The method should not be sensitive to arbitrary indexation (see Tidwell and Mortimer[1]). This means that the two regressions should give similar results.

3.2.3 Determining a joint confidence region

To determine a $100(1 - \alpha)\%$ joint confidence region for r_1 and r_2 we use the fact that the confidence region can be approximated by the contour in the sum-of-squares surface for which

$$S(r_1,r_2) = \hat{S}\left(1 + \frac{2F_{2,N-2}(\alpha)}{N - 2}\right) = S_\alpha \tag{3.9}$$

where $F_{2,N-2}(\alpha)$ is the upper $100\alpha\%$ value of Fisher's F distribution with 2 and N - 2 degrees of freedom; but for $r_2 = r_{2k}$ the sum of squares at any value of r_1 is quadratic in r_1:

$$S(r_1,r_{2k}) = S_k + (r_1 - r_{2k})^2 \, \Sigma \, (v_j^k)^2 \tag{3.10}$$

hence for a fixed value r_{2k} the coordinates of the contour can be obtained by substituting eq. (3.9) in eq. (3.8) to give the coordinates

$$\hat{r}_{1k} \pm \left(\frac{S_\alpha - S_k}{\Sigma \, (v_j^k)^2}\right)^{1/2} , \; r_{2k}$$

Plotting these coordinates for each value of r_{2k} generates the confidence region.

3.3 Applications

3.3.1 Ethylene and vinyl acetate in benzene

Figure 3-2 shows plots of y_{ji} vs. x_{ji} for seven runs of a copolymer reaction of ethylene and vinyl acetate in benzene. The experimental method and conditions can be found elsewhere[11]. It is seen in Figure 3-2 that the straight-line assumption for each run is quite appropriate. Table 3-1 lists the estimates $\overline{Q}_j$, $\hat{\beta}_j$, $\hat{\delta}_j$ and $\tilde{\beta}_j$ for each run.

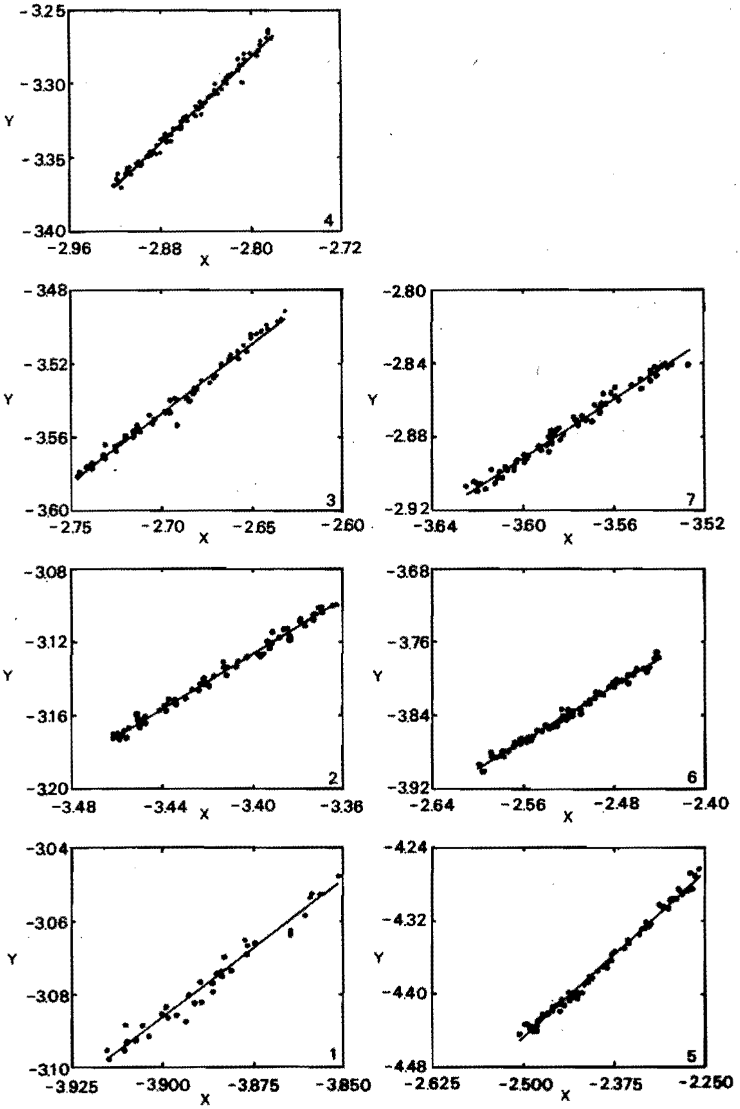

Figure 3-2 y_{ji} (vert.) vs. x_{ji} (hor.); Eth-VAc in benzene.

To determine the parameter estimates we start with r_{2k} = [1.05 (0.05) 2.00] and for each r_2 calculate r_{1k} using eq. (3.8). Table 3-1 also shows the values u_j and v_j for r_2 = 1.40 from which we find $\hat{r}_1(r_2 = 1.40) = (\Sigma\, uv/\Sigma\, v^2) = 0.807$ with $S(0.807, 1.40)$ = 0.00171. The minimum sum of squares, $\hat{S}$ = 0.00157, occurs at $\hat{r}_1$ = 0.797, $\hat{r}_2$ = 1.375 and so S_α = 0.00157[1 + (2/5)(5.79)] = 0.00521, where 5.79 is the upper 5% value of $F_{2,5}$. The 95% confidence region at $r_2 = 1.40$ therefore has coordinates $\{0.807 \pm [(0.00521 - 0.00171)/1.8446]^{1/2}, 1.40\}$, that is (0.763, 1.40) and (0.851, 1.40).

Table 3-1 Summary values for the ethylene (M_1) and vinyl acetate (M_2) in benzene copolymerization data.

					$r_2 = 1.40$	
j	$\hat{\beta}_j$	$1/\hat{\delta}_j$	$\tilde{\beta}_j$	$\bar{Q}_j$	u_j	v_j
1	0.7526	0.7778	0.7651	3.8674	0.5753	0.7342
2	0.7533	0.7609	0.7571	2.2689	0.4849	0.6184
3	0.7531	0.7632	0.7581	0.7356	0.2898	0.3444
4	0.7393	0.7480	0.7436	1.0769	0.3399	0.4348
5	0.7269	0.7338	0.7303	0.2379	0.1198	0.1452
6	0.7519	0.7601	0.7560	0.4603	0.2185	0.2474
7	0.7975	0.8125	0.8050	3.4784	0.6004	0.7135

$\Sigma v_j^2 = 1.8205$, $\Sigma u_j v_j = 1.4697$.

Table 3-2 Copolymerization parameter estimates resulting from the improved curve-fitting I and the linear regression method.

Binary combination[a]		Improved curve-fitting I	Linear regression
Eth-VAc-Bz	r_1	0.79 ± 0.02[b]	0.80 ± 0.02
3.4 MPa	r_2	1.39 ± 0.01	1.37 ± 0.03
VAc-VP	r_1	0.90 ± 0.03	0.91 ± 0.02
3.4 MPa	r_2	1.03 ± 0.03	1.03 ± 0.02
VAc-VPV[c]	r_1	0.88 ± 0.02	0.88 ± 0.01
3.4 MPa	r_2	1.17 ± 0.02	1.17 ± 0.02
VAc-VPV[c]	r_1	0.86 ± 0.01	0.85 ± 0.02
59 MPa	r_2	1.10 ± 0.02	1.08 ± 0.03
VAc-VPV[c]	r_1	0.84 ± 0.01	0.85 ± 0.02
118 MPa	r_2	1.04 ± 0.01	1.09 ± 0.03

[a] Eth = ethylene; VAc = vinyl acetate; VP = vinyl propionate; VPV = vinyl pivalate; Bz = benzene. Copolymerizations at 335 K with *tert*-butyl alcohol as solvent unless otherwise indicated. The experimental data are given elsewhere[11].

[b] Approximate standard deviation.

[c] Evaluation of these results will be published elsewhere[14].

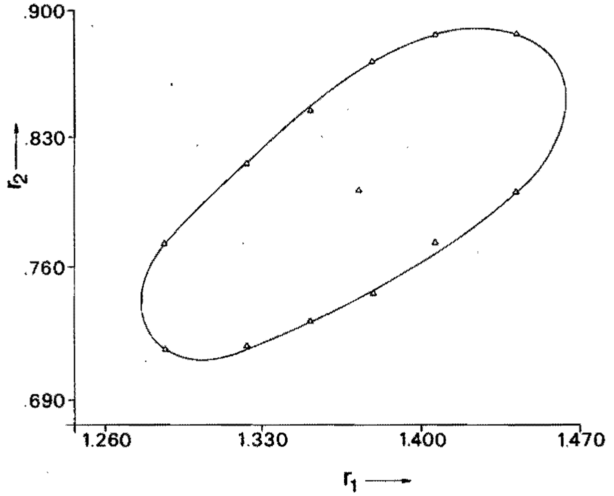

Figure 3-3 Selected points of the 95% confidence sum-of-squares contour for Eth-VAc in benzene.

Figure 3-3 shows the completed 95% contour, which reveals moderate correlation between the two parameters estimates. The contour is very close to an ellipse, which suggests that the estimation situation is not badly affected by nonlinearity.

Estimates for the monomer reactivity ratios were also computed with reindexed monomers. The sensitivity of the estimates to reindexation appears to be small compared with the accuracies of the estimates. This holds as well for the other copolymerizations considered in this chapter. One may use the averages of the estimates, which result from the two regressions, as final estimates of the reactivity ratios.

3.3.2 Other examples

The linear regression method was applied to four other copolymerization data sets and the results are shown in Table 3-2 with the results of the improved curve-fitting I method. The low-pressure experiments show excellent agreement between the two methods, whereas the VAc-VPV copolymerization at 118 MPa shows a sizable difference between the two methods for the value of r_2. Figure 3-4 shows a plot of $\tilde{\beta}_j$ vs. $\overline{Q}_j$ for all five copolymerizations, together with the fitted line given by eq. (3.7). Such a plot is useful in a check for the quality of the design and the goodness of fit and to reveal outliers.

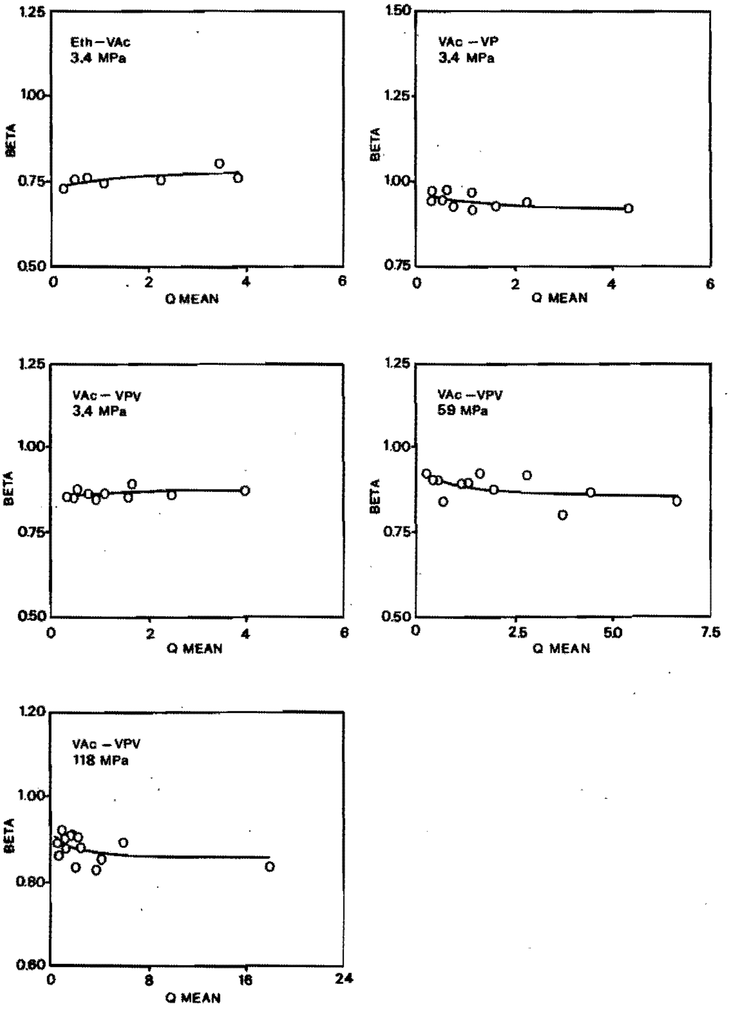

Figure 3-4 $\bar{\beta}$ (vert.) vs. $\bar{Q}$ (hor.); solid line is least-squares fit.

Table 3-3 Copolymerization parameter estimates for the improved curve-fitting I and the linear regression method with $r_1 \cdot r_2 = 1$.

	Copolymerization parameters	Improved curve-fitting I estimates	Linear regression estimates
r_1	0.999	-[a]	0.996 ± 0.010[b]
r_2	1.001	-[a]	0.986 ± 0.016
r_1	0.5	0.494 ± 0.015	0.501 ± 0.013
r_2	2.0	2.055 ± 0.062	2.031 ± 0.054
r_1	0.1	0.125 ± 0.059	0.155 ± 0.038
r_2	10.0	10.083 ± 1.475	7.188 ± 0.667
r_1	0.05	0.191 ± 0.220	0.081 ± 0.041
r_2	20.0	32.999 ± 14.553	8.953 ± 0.989
r_1	10.0	9.957 ± 0.115	9.918 ± 0.101
r_2	0.1	0.098 ± 0.004	0.097 ± 0.005
r_1	20.0	20.116 ± 0.281	19.916 ± 0.216
r_2	0.05	0.049 ± 0.001	0.047 ± 0.003

[a] No convergence for the improved curve-fitting I method.
[b] Approximate standard deviation.

3.4 Range of applicability

The linear regression method is especially suited to cases in which one or two of the r values is close to 1. In these cases the improved curve-fitting I method, due to the numerical instability of the integrated copolymer equation in the neighborhood of r_1 or $r_2 = 1$, tends to converge slowly, as is the case for the copolymerization of vinyl acetate and vinyl propionate at 59 MPa with $r_1 = 0.984 \pm 0.011$ and $r_2 = 0.997 \pm 0.010$ (linear regression estimates)[12]. To cover a wide range of copolymerizations for comparing the two methods and to determine the limits of applicability of the linear regression method copolymerization data were simulated in the following way. For selected values of r_1 and r_2 ten copolymerization experiments by the "sequential sampling" method[4] were simulated with initial monomer feed ratios that varied from 0.4 with steps of 0.4 to 4 and M_2 conversion of 25%. For each experiment starting at 0 the M_2 conversion was increased by a fixed amount of 1% and the corresponding monomer feed ratio was computed from the integrated Alfrey and Mayo equation. Ideal GLC areas (without measurement errors) were computed and these areas were disturbed by a normal error. The standard deviations of the areas

A_1, A_2, and A_s were chosen to be 0.5, 0.5, and 0.75%. These disturbed areas were then used to determine the monomer feed ratio q and the M_2 conversion f_2. The resulting data were then analyzed by the two methods.

Given $r_1 \cdot r_2 = 1$, the Alfrey and Mayo model can be written

$$d \ln n_1 / d \ln n_2 = r_1$$

and the linear regression method seems to be appropriate. The results for some selected cases with $r_1 \cdot r_2 = 1$ are shown in Table 3-3. This table, together with Table 3-4, also serves to illustrate a limitation of the linear regression method. Given a fixed M_2 conversion and $r_2 \gg r_1$ the M_1 conversion is small compared with the measurement error, in which case the regression of $\ln n_2$ on $\ln n_1$ yields unreliable results and the linear regression method breaks down; $r_1 = 0.5$,

Table 3-4 Copolymerization parameter estimates for the improved curve-fitting I and the linear regression method for increasing values of $r_1 \cdot r_2$.

	Copolymerization parameters	$r_1 \cdot r_2$	Improved curve-fitting I estimates	Linear regression estimates
r_1	0	0	-0.017 ± 0.012[a]	0.023 ± 0.008
r_2	2		1.939 ± 0.073	1.957 ± 0.049
r_1	0.01	0.001	0.017 ± 0.006	0.029 ± 0.007
r_2	0.1		0.107 ± 0.006	0.110 ± 0.004
r_1	0.1	0.01	0.084 ± 0.006	0.092 ± 0.007
r_2	0.1		0.098 ± 0.007	0.094 ± 0.004
r_1	0.2	0.1	0.191 ± 0.007	0.200 ± 0.005
r_2	0.5		0.483 ± 0.012	0.489 ± 0.008
r_1	0.4	0.2	0.411 ± 0.008	0.418 ± 0.008
r_2	0.5		0.514 ± 0.014	0.519 ± 0.011
r_1	0.5	2	0.512 ± 0.028	0.518 ± 0.032
r_2	4		3.893 ± 0.191	3.753 ± 0.208
r_1	4	2	4.046 ± 0.050	4.011 ± 0.041
r_2	0.5		0.510 ± 0.015	0.514 ± 0.015
r_1	0.5	5	0.468 ± 0.083	0.438 ± 0.039
r_2	10		9.329 ± 1.223	7.333 ± 0.472
r_1	10	5	9.798 ± 0.174	9.148 ± 0.164
r_2	0.5		0.482 ± 0.017	0.464 ± 0.022
r_1	0.5	10	0.845 ± 0.486	0.211 ± 0.054
r_2	20		34.339 ± 15.535	8.743 ± 1.024
r_1	20	10	19.861 ± 0.525	15.443 ± 0.341
r_2	0.5		0.495 ± 0.020	0.416 ± 0.021

[a] Approximate standard deviation.

r_2 = 10 in Table 3-4 is an example of low M_1 conversion compared with r_1 = 10, r_2 = 0.5. Consequently, the linear regression method performs better in the latter case. Therefore, both the M_1 and M_2 conversions must be large enough, compared with the measurement error, for the linear regression method to be reliable. The improved curve-fitting I method yields more realistic results.

The next limitation concerns the value of $r_1 \cdot r_2$. If $r_1 \cdot r_2 \neq 1$, the relation between ln n_1 and ln n_2 is not a straight line and the results of the linear regression method might be erroneous. Table 3-4 shows the results of the two methods for increasing values of $r_1 \cdot r_2$.

3.5 Conclusions

The linear regression method, given the experimental setup and the measurement errors described, appears to be applicable to a wide range of values of $r_1 \cdot r_2$, that is, when $0.001 < r_1 \cdot r_2 < 2$, provided both M_1 and M_2 conversions are large enough compared with the measurement error. Therefore, the method cannot be used if there is no idea of the possible range of the reactivity ratios to be determined. In general, the range of applicability decreases with increasing measurement error. Copolymerizations with $0.001 < r_1 \cdot r_2 < 2$ constitute 80% of all cases for which there are estimates in the ref. 13.

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Chapter 4

The Influence of Pressure on Free-Radical Copolymerization

Synopsis

The transition state theory is mostly used for the description of the rate constant of a chemical reaction in the liquid phase. According to this theory the kinctic effect of high pressure is primarily dependent on the difference in volume, and with that, on the difference in structure between the activated complex and the reactants. Therefore, also in the present investigation determination of the so-called activation volume $\Delta V^{\#}$ *is a valuable method of revealing relations between structure and reactivity of vinyl monomers. The activation volume is comprehensively illustrated by means of a discussion of the initiation, propagation, and termination reaction in polymerization. However,* $\Delta V^{\#}$ *is not only dependent on the changes in interatomic distances during bond formation and bond breaking on going from the initial state to the transition state, but depends also on the change in interaction between the reactants and the solvent molecules. In polymerization an effect of solvent has to be expected with polar monomers and monomers with functional groups capable of forming hydrogen bonds. In the literature it is concluded that the assumption that sterically hindered reactions are more accelerated by pressure than unhindered ones, due to the fact that the pertaining transition state is located further on the reaction coordinate, is only proved in case of the Menshutkin reaction. It is not clear whether this special pressure effect may be found in polymerization reactions. The most important drawback of the concept of additivity and the Jenner concept (based on the Q-e scheme) for the prediction of the effect of pressure on copolymerization reactions is the fact that neither concept takes into account the reactivity of the radical when*

comparing the reactions of both radicals with the corresponding monomer and the comonomer, respectively. On the other hand, in the new approach based on the Hammond postulate it is assumed that the more reactive the radical the less will be the difference in the experimentally observed volumes of activation (= measure of difference in reactivity). A direct relation is found between reactivity and activation volume. However, none of these three methods seems to be able to give a general description of the pressure-effect in copolymerization. Also, the determination of the range of applicability is very much hampered by the fact that the monomer reactivity ratios in the literature fail to show mutual agreement.

4.1 Introduction

High pressure has become a basic variable and a powerful tool in chemistry, as can be seen from the still growing number of papers published every year. Many of the physical and chemical properties of substances are greatly altered at high pressures, and the study of these changes is of great scientific and technological importance. For example, the polymerization of ethylene has not only proved to be of great economic importance, but has provided a valuable stimulus to chemical research at high pressures and to progress in the design of large-scale high pressure equipment[1]. A summary of the latest advances in the full spectrum of high pressure investigation can be found elsewhere[2,3]. Asano and Le Noble recently published a detailed review on the effect of pressure on reactions in solutions[4]. Furthermore, a review on the effects of pressure on the formation and properties of (co)polymers has to be mentioned[5]. The discussion in this chapter will be restricted to the influence of pressure on chemical reactions in the liquid phase, with emphasis on copolymerization.

Physical properties of the liquid phase affected by high pressure are[1,5-8]: *viscosity* - approximately increases by a factor 2 as the pressure is increased by 100 MPa; *density* - increasing by 5-10% at 100 MPa to 20-40% at 1 GPA; *phase equilibrium* - phase change or phase separation; and *freezing point* - rises between 15 K and 25 K per 100 MPa. The kinetic effects of high pressure are much greater than can be accounted for by the relatively minor increases in concentration and are attributable to changes in the reaction rate constants with pressure. It will be shown that the magnitude of the effect of pressure is determined by the differences between the spatial configurations of the reactant molecules and of the transition state, and by the strength of their respective interactions with neighbouring molecules (e.g., solvent molecules). Studies of reaction rates at elevated pressures are thus of fundamental importance in reaction kinetics. The value of high-pressure investigation of relations between structure and reactivity of vinyl monomers is therefore obvious.

4.2 Effect of pressure on the rate constant

The well-known Arrhenius law[9,10] relates the rate constant of a chemical reaction to the temperature:

$$k = A \exp(-E/RT) \tag{4.1}$$

A is the pre-exponential factor and the exponential term is the fraction of all binary collisions in which the molecules have an energy greater than the activation energy E, necessary for the reaction to occur. This simple equation agrees remarkably well with the experimental results of a great number of studies. However, the precise meaning of the parameters A and E is by no means simple and straightforward[11]. Furthermore, the pressure-dependence of A and E is very complex and no detailed interpretation in terms of the collision theory has yet proved satisfactory[1]. Therefore, the interpretation of the effect of pressure on the rates of reactions in the liquid phase by the transition state theory is preferred.

The transition state theory, worked out independently by Eyring[12] and Evans and Polanyi[13] is also a collision theory. It deals with collisions in a more satisfactory way by taking into account the structures of the reacting molecules and the manner in which they behave on collision. The theory postulates that when two molecules come together in a collision that leads to products, they pass through a configuration of maximum potential energy called the transition state. The basic equation for the reaction rate is:

$$k = (k_B T/h) \exp(-\Delta G^{\#}/RT) \qquad (4.2)$$

in which k_B is Boltzmann's constant, h is Planck's constant and $\Delta G^{\#}$ is the change in Gibb's free energy when the transition state is formed from the reactants. The derivation of this expression can be found in many textbooks[11,14].

The transition state theory involves the hypothesis that the activated complexes are at equilibrium with the reactants, even when the reactants and products are not at equilibrium. Calculation of the rate constant with more detailed theories leads to the conclusion that reactions are satisfactorily interpreted on the equilibrium assumption provided that $\Delta G^{\#}/RT$ has a value of 5 or larger[11]. For the propagation reaction of styrene $\Delta G^{\#}/RT \sim 12$ (E_p = 32.5 kJ/mole[15] and T = 333 K) indicating the validity of the transition state theory for (co)polymerizations.

Differentiation of eq. 4.2 with respect to pressure at constant temperature leads to

$$(\delta \ln k/\delta p)_T = -\Delta V^{\#}/RT \qquad (4.3)$$

in which $\Delta V^{\#}$ is the activation volume representing the difference between the volume of the activated complex and the reactants. Since the activation volume is primarily determined by the atomic positions (= structure of activated complex and reactants) it is more readily understood than the other quantities $\Delta G^{\#}$, $\Delta S^{\#}$, and $\Delta H^{\#}$. It is a valuable method in establishing reaction mechanisms and in investigations relating structure and reactivity of monomers as in the present study.

The application of eq. 4.3 requires the use of pressure-independent concentration units, such as molal units, mole fractions, or moles per liter *at one atmosphere*. There is confusion in the literature about the "corrections" necessary to allow for the apparent fact that compressed solutions have higher concentrations than those at atmospheric pressure. Many papers contain a statement to the effect that compressibility corrections were made. On the other hand, Asano and Le Noble[4] stated that such corrections would be in order only if the solutions were prepared at the high pressures at which they are used, a situation which is not likely to arise frequently.

However, in the present investigation, only effects of pressure on r values have to be considered. Since the r values are the ratios of chain propagation constants, the compressibility terms in $(\delta \ln r/\delta p)_T$ cancel out.

4.3 The activation volume

4.3.1 General introduction

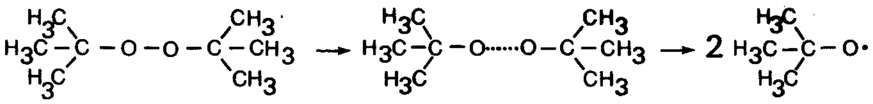
In the transition state theory a chemical reaction is represented as follows:

$$\text{reactants (R)} \rightleftarrows \text{transition state (\#)} \longrightarrow \text{products (P)}$$

The activation volume $\Delta V^{\#}$ is defined by $\Delta V^{\#} = \overline{V}^{\#} - \overline{V}_R$, and the reaction volume, ΔV, is given by $\Delta V = \overline{V}_P - \overline{V}_R$. According to eq. 4.3 the variation of the rate constant k with pressure at constant temperature is governed by the sign and magnitude of $\Delta V^{\#}$. If $\Delta V^{\#}$ is negative, i.e., if the formation of the transition state from the reactants involves a net contraction in volume, the rate constant increases with increasing pressure; and if $\Delta V^{\#}$ is positive k decreases with increasing pressure. This is in contrast to the effect of raising the temperature, which invariably leads to increasing reaction rates. Values of $\Delta V^{\#}$ determined for various reactions range from +20 cm^3/mole to -50 cm^3/mole[1,4,7].

The absolute value of $\Delta V^{\#}$ is determined by the place of the transition state on the reaction coordinate and the area of the reaction cross-section. It is very difficult, perhaps even impossible, to separate these two factors. Important information can be obtained by considering the ratio $\Delta V^{\#}/\Delta V$ and by comparison of similar reactions. However, the results experimentally obtained should be interpreted with great care. As a consequence, the three examples given in the ensuing part of this section only serve to qualitatively illustrate the activation volume $\Delta V^{\#}$.

decomposition of initiator



The decomposition of *tert*-butyl peroxide is assumed to proceed along the axis of a cylinder with a radius of about 0.3 nm[16]. The O-O bond is normally about 0.15 nm long. If we arbitrarily assume that the O-O bond has increased by about 25% when the transition state is reached, the volume difference between the transition and initial state is:

$$\pi \times (0.3)^2 \times (0.25 \times 1.5) \sim 0.01 \text{ nm}^3\text{/molecule}$$

Hence the activation volume will be:

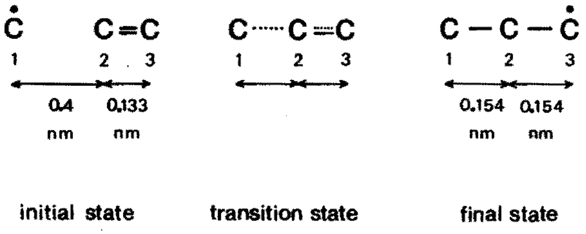
$$\Delta V^{\#} = 0.01 \times (10^{-7})^3 \times 6 \times 10^{23} = 6 \text{ cm}^3\text{/mole}$$

The observed value for this reaction in toluene is +5.4 cm^3/mole.

The picture of initiator decomposition is in fact much more complicated due to the various trajectories possible for radicals receding from the site of a broken bond[7] and the fact that the products through which we become aware that bond scission has occurred point to several competing and successive steps[4].

propagation reaction

The activation volume for the propagation reaction in radical polymerizations has a negative $\Delta V^{\#}$ as will be shown for ethylene. The addition of a monomer to a radical is assumed to proceed along the axis of a cylinder analogously to the decomposition of *tert*-butyl peroxide.



In the initial state C_1 and C_2 are separated by the sum of the van der Waals radii (0.2 nm for $=CH_2$ and $\dot{C}H$[17]) and in the final state the distance is 0.154 nm. The length of the C_2, C_3 bond is increasing from 0.133 nm to 0.154 nm. It is assumed that the radius of the cylinder is equal to that of the van der Waals radius (0.2 nm). The formation of the σ bond then contributes $-\pi \times 0.2^2 \times (0.4-0.154)$ nm^3/molecule = -18.7 cm^3/mole to the total volume change. The formation of a σ bond from the π bond contributes $\pi \times 0.2^2 \times (0.154-0.133)$ nm^3/molecule = $+1.6$ cm^3/mole. Thus, the total volume change, ΔV, amounts to -17.1 cm^3/mole. This rough calculation also serves to illustrate the fact that the radical-monomer contribution to $\Delta V^{\#}$ and ΔV (formation of new σ bond between radical and monomer) is much more important than the contribution of the monomer (transition of a π to a σ-bond). This fits in well with the generally accepted rule that the nature of the radicals determines addition rates to a larger extent than does the nature of the monomers[18-20]. The experimental value of $\Delta V^{\#}$ for the propagation reaction of ethylene is -16 cm^3/mole[21]. The propagation steps in several other free-radical polymerizations have activation volumes in the range -18 to -25 cm^3/mole[22]. At first glance, this points to a late transition state. According to Asano and Le Noble[4] this rather large contraction is likely the result of the large volume requirement of the π bond. The presence of a double bond is known to necessitate a large correction in parachor calculations[7]. However, this conflicts with the potential energy calculations of Evans and coworkers[23]. They concluded that the C_2, C_3 bond remains unchanged in the transition state. Perhaps in the formation of the transition state the surroundings of the double bond are disturbed leading to the observed volume change, while the length of the vinyl bond remains the same.

From the above examples it may be inferred that the termination step in free-radical polymerizations should have a negative $\Delta V^{\#}$. However, the experimentally determined $\Delta V^{\#}$ proves to be quite large and positive[22,24]. This result is explained by the fact that this step is apparently diffusion-controlled, and that diffusion steps through the increasingly viscous medium must surely be pressure-inhibited. The onset of the Trommsdorff effect is often described as the point at which the termination step becomes diffusion-controlled. However, from the foregoing it becomes clear that termination is probably diffusion-controlled to begin with in most if not all polymerization systems. The factors governing the termination reaction in free-radical polymerizations are discussed in more detail by North[25].

A complicating factor may arise from the pressure-dependence of the activation volumes as the compressibility of the transition state almost invariably differs from that of the reactants. Therefore, the pressure must be specified when this quantity is reported. Usually the activation volume refers to zero pressure, $\Delta V_0^{\#}$ (Figure 4-1).

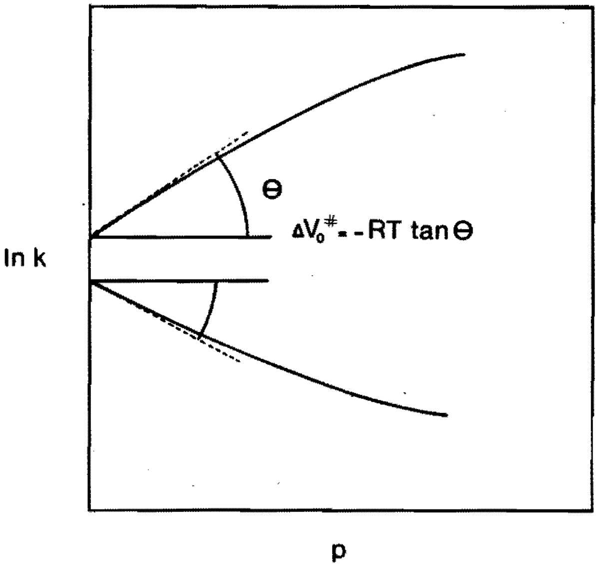


Figure 4-1 Effect of pressure on chemical ration rates.

Generally, it is assumed that volumes of activation are pressure-independent up to 100-150 MPa, although this depends on the absolute magnitude of $\Delta V^{\#}$. As only differences of activation volumes are considered (section 4.4) at pressures up to 118 MPa, the validity of this assumption in the present investigation seems justified.

4.3.2 Effect of solvent on the activation volume

In the preceding section the activation volume $\Delta V^{\#}$ was discussed in terms of the alterations in interatomic distances during bond formation and bond breaking on going from the initial state to the transition state. However, the activation volume experimentally obtained, $\Delta V^{\#}_{exp}$, also reflects the volume change due to the change in interaction between the reactants and the solvent molecules. Therefore, $\Delta V^{\#}_{exp}$, should be regarded as a combination of an intrinsic and a solvation part

$$\Delta V^{\#}_{exp} = \Delta V^{\#}_{intr} + \Delta V^{\#}_{solv}$$

The task of estimating the solvation contribution to the activation volume is equivalent to solving the problem of quantitatively describing the solvent effect on rates of reactions. The latter has not yet been accomplished and, as a consequence, attempts to estimate $\Delta V^{\#}_{solv}$ are but crude approximations.

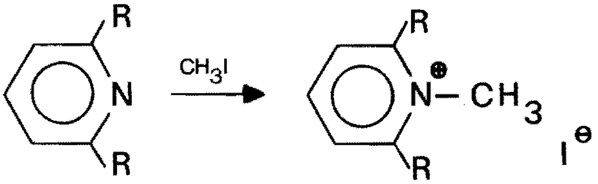
A typical example of the effect of the solvent is ionization. Since this process implies bond fission, one might infer that $\Delta V^{\#}$ and ΔV are positive. However, the development of charges during the reaction increases the strength of the interactions between reactants and solvent, thereby resulting in a negative contribution to $\Delta V^{\#}_{solv}$. Naturally, removal of charges leads to the opposite effect.

In polymerization an effect of solvent has to be expected with polar monomers and monomers with functional groups capable of forming hydrogen bonds.

In chapter 6 the effect of monomer structure, pressure and solvent on the copolymerization of a homologous series of vinyl esters with ethylene as reference monomer and *tert*-butyl alcohol as solvent is discussed. At 3.4 MPa the reactivity of vinyl pivalate is less than expected as compared to the other vinyl esters. This is also reflected in the investigation of the effect of pressure and has been explained by the sterically hindered addition reactions involving at least one vinyl pivalate unit as monomer or macroradical[26-28]. Additional research suggested that the exceptional position of vinyl pivalate is due to a type of interaction with *tert*-butyl alcohol not found in other alcohols. This might be caused by a suitable fit in the solvent lattice as both compounds possess a *tert*-butyl group.

4.3.3 Effect of steric hindrance on the activation volume

In general it is assumed that a sterically hindered reaction has a more negative activation volume, i.e., is more accelerated by pressure, than similar unhindered reactions[4,29]. This phenomenon is most elegantly shown by Le Noble and Asano in their investigation of the Menshutkin reaction for a number of alkyl iodides with 2,6-disubstituted pyridines[29]:



On increasing the steric requirements of the *ortho*-substituents, the reaction rates decrease dramatically, as do the activation volumes. The authors also measured the reaction volumes ΔV and compared them with the activation volumes. If the more negative activation volume is originating from the increasing reaction cross-section only, the fraction $\Delta V^{\#}/\Delta V$ should be a constant. However, $\Delta V^{\#}/\Delta V$ appeared to increase as the hindrance increases. Therefore, Le Noble and Asano suggested that the more negative activation volume is a demonstration of the Hammond postulate[30]. According to this postulate, when two similar reactions differ greatly in the amount of energy released, the more exothermic one will be faster and have an earlier transition state. In other words, in case of increasing steric hindrance, the activation volume becomes more negative, due to the fact that the activated complex is located further along the reaction coordinate; its configuration becomes more product-like. The argument is graphically shown in Figure 4-2.

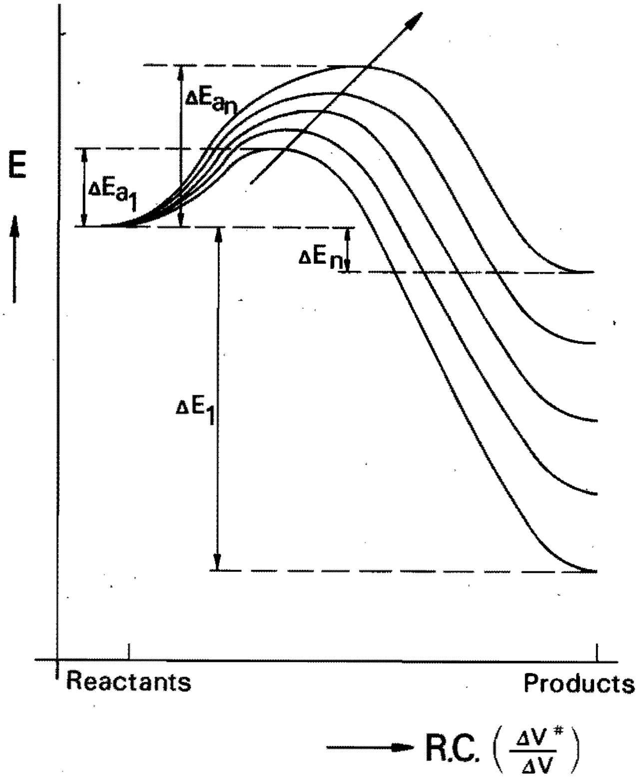


Figure 4-2 The Hammond postulate: a rapid reaction with "reactant-like" transition state vs. a slower reaction with "product-like" activated complex (according to Le Noble and Asano[29]).

It is emphasized that in this way decreasing reactivity is related to a more negative activation volume. This will also be shown in the present investigation (section 4.4 and chapter 6), where the Hammond postulate is used in explaining the influence of pressure on the reactivity of a homologous series of vinyl esters in the copolymerization with ethylene as reference monomer.

Gonikberg et al.[31] also used the Menshutkin reaction to investigate the relation between steric hindrance and activation volume. However, their explanation of the more negative activation volume with "overlapping volumes" due to interpenetration of interfering groups has been strongly criticized[1,3,29,32]. Hamann[32] refers to Amdur[33] who has calculated the energy necessary to compress two methane molecules from 0.43 nm to 0.29 nm. Four $CH_3...CH_3$ interactions require 147 kJ/mole, whereas, for example, the experimental activation energy for the reaction of trimethylamine with *i*-propyl iodide amounts to 57 kJ/mole. Moreover, the explanation conflicts with the concept of parachor[34]. As a consequence, Gonikberg's theory is not accepted as a valuable one.

In addition to the Menshutkin reaction a great number of reactions are believed to show special effects due to steric hindrance[4]. In fact, many were investigated to show that sterically hindered reactions are enhanced more by pressure than unhindered ones. However, according to Asano and Le Noble[4], the results can only be summarized by saying that the large, special pressure effect in hindered Menshutkin reactions has to date found no parallel in other chemistry. The authors also give an explanation based on comparison of the Menshutkin reaction with the superficially similar solvolysis reaction; the latter has a very late transition state already, and the introduction of large substituents cannot induce a further shift. This suggestion could be of major importance in explaining the effect of pressure on steric hindrance in (co)polymerization. In copolymerizations showing penultimate effects due to steric hindrance, it was claimed that high pressure is effective in eliminating the penultimate effect[5,35]. Furthermore, steric hindrance was thought to be reflected in the activation volumes for the copolymerization of vinyl pivalate with ethylene and with vinyl acetate in *tert*-butyl alcohol[27] (see also chapter 6 of this thesis). On the other hand, the propagation steps in several free-radical polymerizations have activation volumes in the range -16 to -25 cm^3/mole[21,22], indicating a late transition state. As a consequence, no special pressure effects should be expected in case of steric hindrance. However, there may be other factors accounting for the large negative activation volume (section 4.3.1). Therefore, for the time being there is little insight, even qualitatively, in the location of the transition state on the reaction coordinate in case of (co)polymerization, and hence in the relation between steric hindrance and activation volume.

4.4 Effect of pressure on free-radical copolymerization

4.4.1 General introduction

Application of high pressure to free-radical (co)polymerization reactions changes them in the following ways[1,5,8]:

- enhancement of the overall-rate;
- increase of molecular mass;
- elevation of the ceiling temperature, according to $dT_c/dP = T_c \cdot \Delta V/\Delta H$ with ΔV and ΔH both negative;
- change of the structure of the (co)polymers (e.g., the stereoregularity).

The interpretation of these phenomena in polymerization requires knowledge of the effect of pressure on the initiation, propagation, and termination reactions. Unfortunately, this information is difficult to obtain. Although three methods have been developed for this purpose[22], they are not considered to be very reliable. The results should be used with great care. Copolymerization has the advantage that only one type of reaction (propagation) has to be considered. On the other hand, the information obtained experimentally is limited to differences in activation volumes.

In most cases the simultaneous polymerization of two monomers can be described by the well-known equation of Alfrey and Mayo[36] (Appendix):

$$\frac{dn_1}{dn_2} = \frac{r_1 q + 1}{r_2/q + 1}$$

with $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The r values are affected by pressure as far as the propagation rate constants are a function of pressure. Although four propagation rate constants have to be considered, the advantage is here that only one type of rate constant is involved for the description of the changing relation between copolymer composition and monomer feed composition with pressure.

Using eq. 4.3 the effect of pressure on the r values is given by

$$\frac{\delta \ln r_1}{\delta p} = \frac{\delta \ln k_{11}}{\delta p} - \frac{\delta \ln k_{12}}{\delta p} = - \frac{\Delta V_{11}^{\#} - \Delta V_{12}^{\#}}{RT}$$

and (4.4)

$$\frac{\delta \ln r_2}{\delta p} = \frac{\delta \ln k_{22}}{\delta p} - \frac{\delta \ln k_{21}}{\delta p} = - \frac{\Delta V_{22}^{\#} - \Delta V_{21}^{\#}}{RT}$$

Therefore, the pressure-dependence of the r values is governed by the difference between the activation volumes for the homopropagation and the cross propagation reactions. The absolute values of these differences are always lower than 10 cm^3/mole[5].

4.4.2 Prediction of the directional effect of pressure on *r* values in free-radical copolymerization

An investigator has only done half the job, if he only tries to interpret and correlate his results. Much can be learned from the *prediction* how this system will behave under certain conditions and comparison with experimental data. There are a number of attempts to predict the directional effect of pressure on r values in free-radical copolymerization. Asai and Imoto[37] have remarked that pressure influences r values if each monomer has a double bond conjugated to another multiple bond (C=O, C≡N, ...) or to an aromatic group (e.g., in styrene). An interpretation based on the *Q–e* scheme[38] is discussed and further developed by Jenner and Aieche[39,40]. Furthermore, van der Meer et al.[41] proposed a simple concept based on the additivity of activation volumes. In this section a new method will be discussed based on the Hammond postulate.

In this concept the activation volume for the reaction of a radical with a monomer is expressed as the sum of the partial activation volumes of the radical and the monomer. In the first instance, it is assumed that these partial activation volumes are characteristic of the monomers and the radicals, regardless of the combination involved. Hence

$$\begin{aligned}
\Delta V_{11}{}^{\#} &= \Delta V_{1}\bullet{}^{\#} + \Delta V_{1}{}^{\#} \\
\Delta V_{12}{}^{\#} &= \Delta V_{1}\bullet{}^{\#} + \Delta V_{2}{}^{\#} \\
\Delta V_{22} &= \Delta V_{2}\bullet{}^{\#} + \Delta V_{2}{}^{\#} \\
\Delta V_{21} &= \Delta V_{2}\bullet{}^{\#} + \Delta V_{1}{}^{\#}
\end{aligned}$$

Combination with eq. 4.4 gives:

$$\frac{\delta \ln r_1}{\delta p} = - \frac{\Delta V_{11}{}^{\#} - \Delta V_{12}{}^{\#}}{RT} = - \frac{\Delta V_{1}{}^{\#} - \Delta V_{2}{}^{\#}}{RT} = - \frac{a}{RT}$$

and

$$\frac{\delta \ln r_2}{\delta p} = - \frac{\Delta V_{22}{}^{\#} - \Delta V_{21}{}^{\#}}{RT} = - \frac{\Delta V_{2}{}^{\#} - \Delta V_{1}{}^{\#}}{RT} = + \frac{a}{RT}$$

As the radical contributions cancel out, the pressure-dependence of the r values is described by the difference of partial monomer activation volumes. Furthermore, if this concept is valid $r_1 \cdot r_2$ does not change with pressure, because

$$\frac{\delta \ln (r_1 \cdot r_2)}{\delta p} = \frac{-a + a}{RT} = 0$$

Even when the activation volume cannot be described as the sum of two independent partial volumes, one may at least expect $\delta \ln r_1/\delta p$ and $\delta \ln r_2/\delta p$ to be of opposite sign.

There is an important implication of the additivity scheme[27]. The effect of pressure on the copolymerization of M_1 and M_2 is determined by: $\Delta V_1^{\#} - \Delta V_2^{\#} = a$. Analogously, for the system M_1, M_3: $\Delta V_1^{\#} - \Delta V_3^{\#} = b$. As a consequence, this enables the prediction of the effect of pressure on the copolymerization of M_2 with M_3: $b - a = \Delta V_2^{\#} - \Delta V_3^{\#}$.

concept based on the *Q-e* scheme

The Q–e scheme describes monomer reactivity in terms of resonance stabilization (Q) and polarity (e), with neglect of steric factors, aiming to predict the r values of monomer pairs (see also sections 2.4.2 and 2.4.4). The basic expressions are:

$$r_1 = Q_1/Q_2 \exp[-e_1(e_1-e_2)]$$

$$r_2 = Q_2/Q_1 \exp[-e_2(e_2-e_1)]$$

and

$$r_1 \cdot r_2 = \pi = \exp[-(e_1-e_2)^2]$$

Jenner et al.[39,40] simply determined Q and e values for a great number of monomers at 0.1 MPa and 300 MPa from their own experiments as well as from r values found in the literature. The experimental r values at 300 MPa then were compared with the predicted r values. According to the authors, satisfactory agreement was obtained between predicted and observed direction of changes in r values as a result of pressure variations (but see section 4.4.3).

concept based on the Hammond postulate

In section 4.3.3 the effect of steric hindrance on the Menshutkin reaction was shown to be a demonstration of the Hammond postulate. According to this postulate, when two similar reactions differ greatly in the amount of energy released, the more exothermic one will be faster and have an earlier transition state. In this way decreasing reactivity is related to a more negative activation volume because the pertaining activated complex becomes more product-like. It should be emphasized that in copolymerization the condition of similar reactions is most elegantly fulfilled as the reactions of two vinyl monomers with the same radical are compared:

$$\frac{\sim M_1\cdot + M_1 \ (k_{11})}{\sim M_1\cdot + M_2 \ (k_{12})} \qquad \frac{\sim M_2\cdot + M_2 \ (k_{22})}{\sim M_2\cdot + M_1 \ (k_{21})}$$

$$r_1 = k_{11}/k_{12} \qquad r_2 = k_{22}/k_{21}$$

The validity of the Hammond postulate in copolymerization is furthermore supported by the results of an investigation of the factors influencing the activation energies of reactions involving double bonds and radicals[23]. The authors stated: "An important generalization is observed - that the activation energy is lower the more exothermic the addition reaction, that is the stronger the bond formed between the radical and the carbon center. These results are to be applied to cases of initiation of polymerization and to chain propagation reactions".

The effect of pressure on the r values is given by eq. 4.4: $\Delta V_{11}^{\#} - \Delta V_{12}^{\#}$ is denoted as A and $\Delta V_{22}^{\#} - \Delta V_{21}^{\#}$ as B. According to the Hammond postulate the activation volume for the homopropagation reaction should differ from that for the cross propagation reaction due to the difference in reactivity of M_1 and M_2 towards the radical. As the difference in reactivity is increased the absolute values for A and B will also increase. As a consequence, A and B are characteristic of the monomer pair involved. Therefore, determination of the effect of pressure is a powerful tool in the investigation of relations between structure and reactivity of vinyl monomers. In case of the copolymerization of a homologous series of monomers M_2 with a reference M_1, the homopropagation reaction of M_1 recurs in all combinations. Therefore, the value of A is dependent on the difference in reactivity of the monomers M_2 and M_1 with respect to $\sim M_1\cdot$. As a result, if various monomers M_2, M_3 ... are each copolymerized with M_1, the effect of pressure on r_1 for a monomer pair can be predicted. By the same token the effect of pressure on r_2 can be discussed. If there were no influence of the radical reactivity the absolute values of A and B would be equal (see concept of additivity). However, this situation is not frequently met in practice. The more reactive the radical, the less the difference in activation volumes (= difference in reactivity), experimentally obtained. As the reactivity of $\sim M_1\cdot$ is different from the reactivity of $\sim M_2\cdot$, the absolute values of A and B will not be the same.

The main features in using the Hammond postulate in the interpretation and prediction of the pressure-effect on r values are:

- the r values move towards unity, as the slower monomer addition is more accelerated by pressure, i.e., has a more negative $\Delta V^{\#}$, than the faster reaction;
- the nature of the radicals determines addition rates to a larger extent than does the nature of the monomers, showing up in different values of $|A|$ and $|B|$.

4.4.3 Discussion and conclusions

Since the development of the Alfrey-Mayo scheme the r values of a great number of monomer pairs have been determined[42]. Only very few have been investigated at elevated pressures[1,5,39,40,42,43], despite the fact that this is of much theoretical and technological importance. In principle Young's tabulation[42] provides a rich source of information on the relative reactivity of monomers. However, the r values fail to show mutual agreement, and it is very difficult to choose the right ones. This may be partly explained by the different experimental conditions (pressure, solvent, concentration, etc.), but is mainly due to the way of evaluating the r values from the experimental data (see also section 2.3). No uniform method for their determination has been developed until recently[44]. As the various procedures are not equally reliable, the veracity of the vast number of published data is just as varied. As a consequence, the results should be handled with great care. The same holds, perhaps even more, for the r values obtained at high pressure. As a consequence, the determination of the validity of any scheme developed to predict the effect of pressure on r values, by considering the r values found in the literature, should be judged against this background.

None of the three methods described here seems to be able to give an all-inclusive interpretation of the pressure-effect on r values. In the additivity concept the r values will change with increasing pressure in opposite direction with $r_1 \cdot r_2$ = constant. Although this has been found in only a few examples[27,41], the statement of the authors "at least it may be expected that $\delta \ln r_1/\delta p$ and $\delta \ln r_2/\delta p$ are opposite in sign", seems to be valid in many cases. However, this conflicts with the interpretation based on the Hammond postulate for those monomer having both r values < 1. According to this postulate the r values tend to move towards unity with increasing pressure, whereas the concept of additivity predicts that one r becomes smaller. On the other hand, the concept based on the Hammond postulate is able to explain the influence of pressure on the reactivity of a homologous series of vinyl esters in the copolymerization with ethylene as reference monomer, as will be discussed in chapter 6. At first glance, the concept based on the *Q-e* scheme[39,40] should cover these cases, because it is an empirical concept, in principle permitting both the r values and the $r_1 \cdot r_2$ product to shift in either direction. However, in addition to the general comments stated in section 2.4.4, some specific remarks have to be made.

- The authors used several monomers for which the Alfrey-Mayo copolymerization model is presumably inappropriate (isopropenyl acetate, α-methylstyrene).
- The r values for a number of monomer pairs (e.g., methyl acrylate-crotonaldehyde) are much too disparate to be evaluated reliably. In the experimental determination the conversion of the less reactive monomer probably lies within experimental error, leading to erroneous results[45] (see also chapter 3).
- It is not clear why methyl acrylate instead of styrene was chosen as zero point of the *Q-e* scale. In our opinion the method should not be sensitive to this. On the other hand this substitution may lead to values for Q and e which are not physically realistic.

The above reinforces our opinion that the method is not as reliable as claimed by the authors.

In section 2.4.4 it was shown that a reliable description of reactivity should take into account contributions which depend on the structures of both monomer and corresponding radical. The same holds for a reliable description of the effect of pressure on the reactivity of vinyl monomers. This condition is only fulfilled in the concept based on the Hammond postulate and strongly supports the use of this concept. However, to gain more insight in the directional effect of pressure on *r* values additional research is necessary with carefully chosen monomers, such as ethylene-vinyl esters (chapter 6) and styrene-(meth)acrylates-vinyl ketones (chapter 7), investigated under standard conditions. Furthermore the *r* values should be evaluated by one of the reliable methods, newly developed[44,45].

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Chapter 5

A Novel Method of Measuring Monomer Reactivity Ratios under High-Pressure Conditions

Synopsis

Mostly, high-pressure copolymerizations are investigated by means of the laborious isolation, purification, and analysis of the copolymer formed. Significant improvement can be obtained by repeated gas chromatographic analysis of the reaction mixture during the low-pressure stages preceding and succeeding the high-pressure stage ("quenching" and "sandwich" method). However, in this way only two, although very accurate, data points are obtained. In the existing methods of continual analysis of reaction mixtures under high pressure, at the risk of phase-separation the sample is collected and subsequently analyzed. These methods cannot be used in case of volatile reactants or products. Therefore, an on-line sampling technique is developed, which is particularly valuable when one of the reactants or products is a gas. In addition a great number of data points per experiment can be obtained. The new "sequential sampling" method has been tested for the copolymerization of ethylene with vinyl propionate at 118 MPa and 335 K with tert-*butyl alcohol as solvent. The results are compared with those obtained by means of the "quenching" method. It appears that the "sequential sampling" method is the most suitable technique for the determination of high-pressure monomer reactivity ratios. Moreover, the technique is not restricted to copolymerization reactions nor to gas chromatography which was used to analyze the reaction mixture.*

5.1 Introduction

Gas-liquid chromatographic (GLC) analysis allows a direct and accurate determination of the changing feed composition throughout a copolymerization reaction up to relatively high conversions (ca. 40%)[1-9]. This experimental technique has many advantages compared to the more troublesome and inaccurate copolymer compositional analysis[10]. Generally, samples are taken from the reaction mixture and injected into the gas chromatograph by means of a syringe. There are two methods permitting direct sampling from the reaction mixture by means of a specially constructed sampling device[5,8,9]. The on-line GLC technique, described by German and Heikens[5], is particularly useful when gaseous monomers are involved in the copolymerization reaction. However, the use of the special sampling disk valve[11] is restricted to pressures of about 4 MPa. For copolymerizations at higher pressures van der Meer and German[8] therefore resorted to the "quenching" and the "sandwich" method. Both methods are based on GLC analysis of the reaction mixture under low-pressure conditions just preceding and succeeding the high-pressure stage. The authors slightly prefer the "quenching" method, in which a great number of samples are taken from the noncopolymerizing reaction mixture at the two low-pressure stages. In the literature frequently a "quenching"-like method is used based on the laborious isolation, purification and analysis of the copolymer formed.

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

5.2 Experimental

The high-pressure apparatus is schematically shown in Figure 5-1 and will be discussed in the subsequent sections.

5.2.1 Reactor

The high-pressure reactor used in the present investigation is an Autoclave Engineers autoclave type No. E74-2988. Parts of the reactor which may come into contact with the reaction mixture are made from stainless steel A286. The maximum working pressure is 250 MPa at 350 K. A Teflon piston separates the reaction chamber from a compartment filled with the pressurizing liquid isopropyl alcohol. This compartment is connected with the pressure control system. The reaction volume is approximately 0.75 dm^3. By means of a magnetic stirrer at 500 rpm an almost ideal mixing is obtained in the reaction chamber[16].

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

The pressure control system is assembled from the following components: a high-pressure piston pump with remotely controllable piston stroke, type Lewa HM1-H1; a Foxboro type M/45 pneumatic pressure transmitter; a Foxboro Consotrol model 52A pneumatic controller; and a pneumatically actuated Annin model 5061 "Wee Willie" Domoter valve. The pressure control system is suited for pressures up to 200 MPa.

5.2.2 Sampling

The special sampling disk valve is described elsewhere[11]. The gas chromatographic system used is the same as described previously[5].

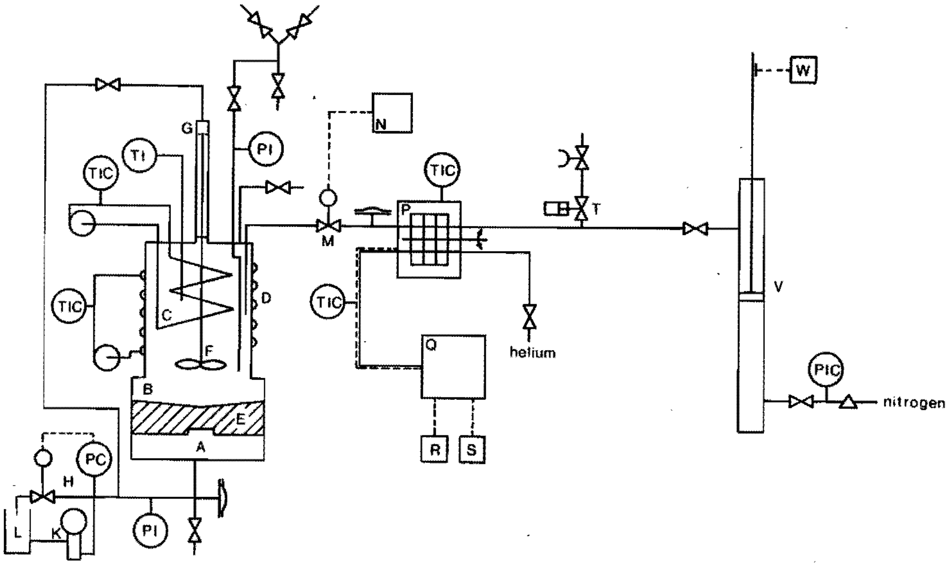

Figure 5-1 Simplified scheme of the high-pressure apparatus used in the present investigation. A, compartment connected with pressure control system; B, reaction chamber; C, internal heating coil; D, external heating coil; E, Teflon piston; F, internal stirrer; G, magnetic stirrer; H, pressure control system; K, piston pump; L, supply flask; M, metering valve; N, stepping motor; P, sample device; Q, gas chromatograph; R, electronic integrator; S, recorder; T, pneumatically actuated valve; V, cylinder with free-moving piston; W, piston shaft displacement transducer. Abbreviations in circles: T, temperature; P, pressure; I, indicator; C, controller.

''sequential sampling'' method

The high-pressure metering valve (M, Autoclave Engineers type No. 60VRM6872) can be opened and closed at a controlled rate (between one turn in 7 seconds and one turn in 20 minutes). This is achieved by means of a SLO-SYN synchronous stepping motor type M061-FCOB, provided with an 20:1 reduction gear and a slip coupling, in combination with a SLO-SYN translator (N). When reaction mixture is sampled from the reactor, the pressure decreases about 1.0-1.5 MPa, but is quickly restored by the pressure control system. In case of exclusively liquid monomers, after adequate flushing a representative sample of the reaction mixture can be collected and analyzed. However, this is not possible in case of volatile components, while in addition the reaction mixture has to be kept homogeneous. Therefore, the reaction mixture is led through the sampling device (P) into a cylinder (V). The total amount of reaction mixture is determined by the need of amply flushing the sampling system (approx. 5 cm^3 in our experiments). In cylinder V the piston begins to move as soon as the pressure exceeds 3 MPa. This pressure is maintained by means of the pressure of the N_2-gas at the lower side of the piston. In this way, phase-separation can be avoided. The quantity of reaction mixture in the cylinder is determined by means of the displacement of the piston shaft (W). As soon as enough reaction mixture is flushed through the sample chamber, valve M is closed and a sample of 2 μl is injected into the column. The mixture collected in cylinder V can be drained through valve T. In order to improve repeatability, the entire sampling cycle is automated. A rupture disk protects the sampling system against excess pressure.

In this way a set of GLC observations of the copolymerizing reaction mixture at high pressure can be obtained (see Figure 5-2(I)).

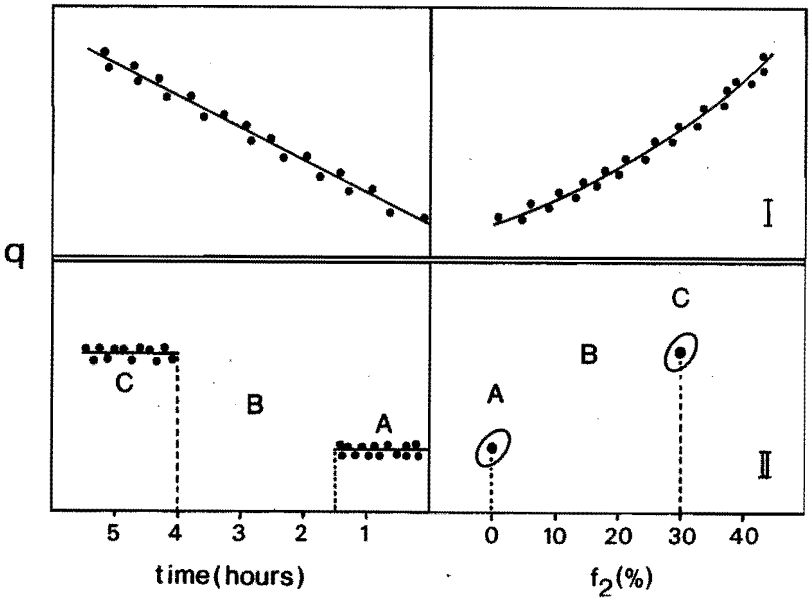

Figure 5-2 Plots of the monomer feed ratio q versus both the reaction time and the degree of conversion f_2 for a "sequential sampling" experiment (I) and a "quenching" experiment (II).

"quenching" method

In this method three different stages have to be distinguished, as schematically shown in Figure 5-2(II). During the first stage (A) the pressure is 3.4 MPa and the temperature is approximately 320 K. Under these conditions no reaction occurs and a set of GLC observations is made. In stage B at the desired pressure and temperature the copolymerization is allowed to continue for a fixed time. The reaction is quenched by a quick drop of pressure and temperature. Finally, in stage C a second set of GLC observations is made from the noncopolymerizing reaction mixture. In this way the monomer feed composition before and after the high-pressure stage is determined very accurately.

5.2.3 Copolymerization

The copolymerization of ethylene (Eth) with vinyl propionate (VP) in *tert*-butyl alcohol (TBA) with α,α'-azobisisobutyronitrile (AIBN) as free-radical initiator has been carried out with both the "sequential sampling" and the "quenching" technique. The purification and physical properties of the reagents are given elsewhere[17]. The gas chromatographic conditions were: column length, 2m; column temperature, 325 K; stationary phase, 15% by wt of a mixture of 30% by wt of diglycerol and 70% by wt of quadrol on chromosorb P-AW 60-80 mesh (Johns Manville); sample size, 2 μl. The details of the experiments are given in the Tables 5-1 and 5-2. The monomer reactivity ratios have been evaluated by means of the improved curve-fitting I method[10]. This procedure, based on the integrated copolymer equation (eq. 2.2), considers experimental errors in *both* measured variables. In addition the r values are compared with those obtained with the recently developed linear regression method[18] (see chapter 3).

Table 5-1 Experimental conditions of the copolymerization of ethylene (M_1) with vinyl propionate (M_2) at 118 MPa and 335 K with *tert*-butyl alcohol as solvent by means of the "quenching" method.

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

Table 5-2 Experimental conditions of the copolymerization of ethylene (M_1) with vinyl propionate (M_2) at 118 MPa and 335 K with *tert*-butyl alcohol as solvent by means of the "sequential sampling" method.

Initial monomer feed ratio q_0	Final monomer feed ratio	Conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mole/dm^3)	Initiator concentration (mmole/dm^3)
3.896	4.069	14.1	12	1.5	3.7
3.000	3.169	17.7	15	1.8	4.2
2.816	3.037	23.7	21	1.7	2.7
2.760	2.989	24.8	18	1.4	3.3
2.336	2.464	17.6	12	1.5	3.3
1.819	2.000	29.7	21	1.3	2.8
1.348	1.455	25.2	19	1.1	5.6
1.342	1.475	30.1	20	1.4	2.8
1.081	1.179	28.5	13	1.6	4.7
1.022	1.116	30.0	12	1.9	3.7
0.940	1.018	27.0	11	1.8	3.7
0.939	1.013	26.3	14	1.8	4.2
0.936	1.021	29.1	11	1.8	4.7
0.581	0.631	28.8	9	0.9	3.3
0.565	0.618	31.3	12	1.4	2.7
0.555	0.604	29.3	14	1.4	2.7
0.482	0.531	33.5	13	1.6	2.8

5.3 Results and discussion

The calculated r values for the Eth-VP copolymerization at 118 MPa and 335 K with the "sequential sampling" and the "quenching" method are given in Table 5-3.

Table 5-3 Monomer reactivity ratios for the ethylene (M_1)-vinyl propionate (M_2) copolymerization in *tert*-butyl alcohol at 118 MPa and 335 K with the "sequential sampling" and "quenching" method calculated by means of the improved curve-fitting I[10] and the linear regression procedure[18].

Calculation procedure		"sequential sampling" method	"quenching" method
Improved curve-fitting I	r_1	0.69 ± 0.02[a]	0.67 ± 0.01[a]
	r_2	1.27 ± 0.03	1.28 ± 0.02
Linear regression	r_1	0.68 ± 0.02	0.68 ± 0.02
	r_2	1.26 ± 0.03	1.30 ± 0.03

[a] Approximate standard deviations.

The 95%-confidence regions for the r values obtained by means of the improved curve-fitting I procedure are shown in Figure 5-3. It may be concluded that both the experimental methods give the same results within experimental error for both the calculation procedures. The r values calculated by means of the linear regression procedure are not solely added to emphasize the power of this very simple method but also for reasons of comparison of the results of both methods. The mathematical framework of the linear regression method is basically different from that of the improved curve-fitting I method. Therefore, the agreement of the corresponding r values for both calculation procedures corroborates the validity of the Alfrey-Mayo scheme[19,20] to describe the copolymerization of Eth with VP for both the experimental methods. In addition an objective mathematical F test[21], based on the statistical comparison of residual sums of squares, can be used, with which it is possible to check the goodness of fit of any copolymerization scheme. In this model-fitting test the calculated $F_{\nu 2}^{\nu 1}$ is compared with the critical value $F_{\nu 2}^{\nu 1}$ (α). A large value of

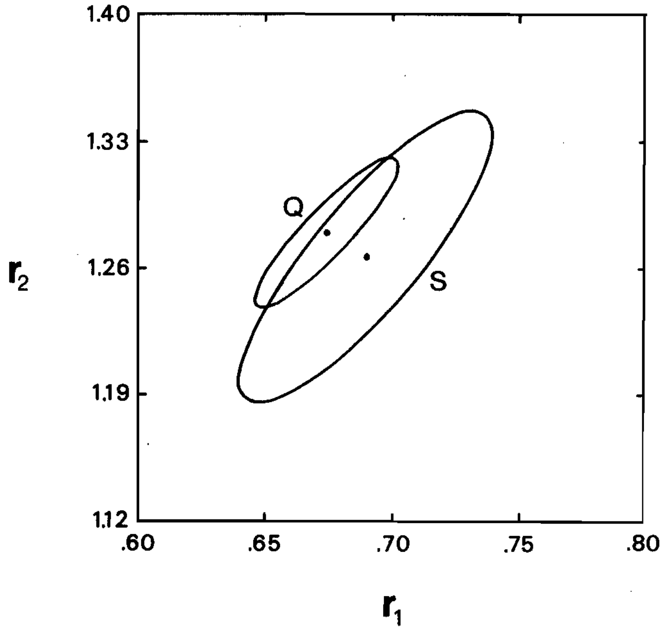

Figure 5-3 Calculated confidence region (α = 95%) for the copolymerization of ethylene (M_1) with vinyl propionate (M_2) at 118 MPa and 335 K with *tert*-butyl alcohol as solvent by means of the "sequential sampling" method (S) and the "quenching" method (Q).

$F^{\nu 1}_{\nu 2}$ leads to the conclusion that the particular scheme is not appropriate to describe the observed kinetic behavior. However, in applying the *F* test to the present Eth-VP copolymerization there is a contradiction between the two experimental methods. In case of the "sequential sampling" method the *F* test justifies application of the Alfrey-Mayo scheme ($F^{15}_{213} = 0.70 < F^{15}_{213}\ (0.05) = 1.67$), whereas in the "quenching" method the *F* test ($F^{11}_{270} = 3.84 > F^{11}_{270}\ (0.05) = 1.79$) leads to rejection of the Alfrey-Mayo scheme. This is also found in other copolymerizations investigated by means of the "quenching" method[22]. Furthermore, it is remarkable that in case of the improved curve-fitting I procedure the standard deviations, and with that the area of the ellipse, are greater in the "sequential sampling" method than in the "quenching" method.

To determine whether these are systematic discrepancies, copolymerization data were simulated in the following way. For a number of selected r values ten copolymerization experiments were simulated with initial monomer feed ratios that varied from 0.4 with steps of 0.4 to 4.0 and M_2 conversion of 25%. In addition the number of observations per experiment was varied. In case of the "quenching" method the number of observations were equally distributed among the two low-pressure stages. For each experiment the M_2 conversion was increased from zero by equal amounts (depending on the number of observations) and the corresponding monomer feed ratio was computed from the integrated Alfrey-Mayo equation (eq. 2.2). Ideal GLC areas (without measurement errors) were computed and those areas were disturbed by a normal error. The standard deviations of the areas of the two monomers and the solvent were chosen 0.5, 0.5, and 0.75%, respectively. The areas thus obtained were then used to recalculate the monomer feed ratio q and the M_2 conversion f_2. The resulting data were then analyzed by the improved curve-fitting I procedure. The results are given in Table 5-4.

Table 5-4 Effect of experimental technique and number of observations on copolymerization parameter estimates calculated by means of the improved curve-fitting I method.

Copolymerization parameters		Number of observations	"Sequential sampling" method			"Quenching" method		
r_1	r_2		r_1	r_2	$F^{\nu 1}_{\nu 2}$ [a]	r_1	r_2	$F^{\nu 1}_{\nu 2}$ [a]
		140	0.204 ± 0.009	0.488 ± 0.016	0.63	0.199 ± 0.006	0.497 ± 0.010	0.48
0.2	0.5	260	0.191 ± 0.007	0.483 ± 0.012	0.60	0.198 ± 0.004	0.496 ± 0.007	0.94
		400	0.211 ± 0.006	0.516 ± 0.010	0.91	0.205 ± 0.004	0.510 ± 0.006	1.03
		140	0.518 ± 0.020	2.127 ± 0.082	0.53	0.502 ± 0.012	2.035 ± 0.048	0.63
0.5	2.0	260	0.494 ± 0.015	2.055 ± 0.062	0.73	0.495 ± 0.009	2.019 ± 0.036	0.95
		400	0.493 ± 0.012	2.013 ± 0.048	1.23	0.502 ± 0.007	2.028 ± 0.029	0.82
		140	3.896 ± 0.064	0.459 ± 0.020	0.23	3.962 ± 0.041	0.477 ± 0.013	0.41
4.0	0.5	260	4.046 ± 0.050	0.510 ± 0.015	0.69	4.013 ± 0.030	0.501 ± 0.009	0.70
		400	3.924 ± 0.039	0.480 ± 0.012	0.43	3.954 ± 0.024	0.489 ± 0.007	0.87

[a] In case of 140 observations $F^{\nu 1}_{\nu 2}$ (0.05) = 2.02 else $F^{\nu 1}_{\nu 2}$ (0.05) = 1.94.

From this Table it can be seen that the precision of both techniques improves as the number of observations increases. However, in the case of an equal number of observations the *r* values are obtained with greater precision by means of the "quenching" method than by means of the "sequential sampling" method, which argues for the former method. An explanation may be found in the different design of the experiments (see Figure 5-2). In the "sequential sampling" method the observations are distributed along the entire curve, whereas in the "quenching" method the observations are located at the extremities of the line.

In the linear regression method two sources of imprecision determine the standard deviations (Table 3-5): the experimental error and the approximation error which originates from the use of $\bar{q}$ in eq. 3.6.

It is remarkable that in case of the simulated "quenching" experiments the *F* test does not lead to the rejection of the Alfrey-Mayo scheme, in contrast with the real experiments[22]. This remains unexplained.

The fact that in practice most copolymerizations can be described by the Alfrey-Mayo scheme supports the "quenching" method due to its greater precision as compared to the "sequential sampling" method. However, it seems justified to state that in case there is any doubt in using the Alfrey-Mayo scheme for the relevant copolymerization, the "quenching" method is less reliable for determining the best extended copolymerization scheme describing the kinetics. This leads to the conclusion, that the results of many investigations involving extended schemes, that are based on the "quenching"-like procedure of copolymer compositional analysis[23] are less well founded than the authors have claimed. Moreover, there are a number of reasons why the "sequential sampling" method is preferred over the "quenching" method.

On-line analysis of reaction mixtures yields a great number of observations per experiment. On the other hand, by means of the "quenching" method only two, although very accurate, observations are obtained.

In the "quenching" method the first kinetic stage just after the induction period is included, where the initial pattern of monomer consumption is likely to be uncharacteristic of the reaction. This may cause systematic deviations from the Alfrey-Mayo scheme[8,24]. In the "sequential sampling" method this stage can be omitted.

The "quenching" method cannot be used for reactions with a low energy of activation. On the contrary, in the "sequential sampling" method it is possible to go directly to the desired pressure and temperature, and start sampling.

In conclusion, we are at opinion that the "sequential sampling" technique described in this chapter is a valuable method for the GLC determination of high-pressure monomer reactivity ratios. In addition, this method is not restricted to copolymerization but is widely applicable in combination with various other analytical techniques. Furthermore, the method is particularly suitable in case of volatile reactants or products.

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Chapter 6

Relations between Structure and Reactivity of a Homologous Series of Vinyl Esters

Synopsis

The effect of monomer structure, pressure, and solvent on the reactivity of a homologous series of vinyl esters ($RCOOCH = CH_2$) has been thoroughly investigated in our laboratory. The relative reactivities appeared to increase with the decreasing electron-withdrawing ability of the ester group. The low vinyl pivalate (R = tert-*butyl) reactivity as compared to the reactivities of the other vinyl esters was explained by means of sterically hindered addition reactions. However, additional research described in this chapter, points to an explanation based on the role of the solvent* tert-*butyl alcohol. Furthermore, a striking correlation was observed between reactivities and activation volumes. It was found that the effects of pressure on these copolymerizations are completely consistent with, and thus may be predicted by the Hammond postulate.*

6.1 Introduction

Earlier investigations in our laboratory[1-13] have revealed important effects of pressure, monomer structure, and solvent on reactivity in case of a homologous series of vinyl esters. The need for consistent models describing the above effects is clearly indicated by that work and, therefore, it is the aim of the present chapter to evaluate improved models. Before presenting these models and their applications to earlier and new results, a summary will be given of the "state of the art" at the start of the present investigation.

effect of monomer structure[1,3,4,8,11]

The effect of the alkyl group R on the relative reactivity of a homologous series of vinyl esters (Table 6-1), has been studied by means of the copolymerization with ethylene (Eth) and with vinyl acetate (VAc) as reference monomers, in *tert*-butyl alcohol (TBA) at 335 K and 3.4 MPa. The results are given in Table 6-2.

Table 6-1 Vinyl esters, $RCOOCH=CH_2$.

Vinyl ester	R	Abbreviation
Vinyl acetate	CH_3	VAc
Vinyl propionate	C_2H_5	VP
Vinyl butyrate	C_3H_7	VB
Vinyl isobutyrate	iso-C_3H_7	ViB
Vinyl pivalate	*tert*-C_4H_9	VPV

Table 6-2 Monomer reactivity ratios for the copolymerization of a homologous series of vinyl esters with ethylene[8] and with vinyl acetate[11] as reference monomers in *tert*-butyl alcohol at 335 K and 3.4 MPa calculated by means of the improved curve-fitting I method[13].

Vinyl ester	Ethylene as reference monomer[a]			Vinyl acetate as reference monomer[a]		
	r_1	r_2	$1/r_1$	r_1	r_2	$1/r_1$
VAc	0.74 ± 0.01	1.50 ± 0.01	1.35	1.00[b]	1.00[b]	1.00[b]
VP	0.67 ± 0.01	1.50 ± 0.01	1.48	0.90 ± 0.03	1.03 ± 0.03	1.11
VB	0.70 ± 0.01	1.51 ± 0.02	1.44	0.90 ± 0.01	1.03 ± 0.01	1.11
ViB	0.61 ± 0.01	1.49 ± 0.02	1.64	0.81 ± 0.02	1.05 ± 0.03	1.23
VPV	0.64 ± 0.01	1.49 ± 0.01	1.55	0.88 ± 0.02	1.17 ± 0.02	1.14

[a] Reference monomer is M_1.

[b] Hypothetical copolymerization.

The Taft relation was used to decide whether the reactivity of the vinyl esters is affected by polar factors or steric factors, or by both.

$$\log\,(1/r_1) = \rho^*\,\sigma^* + \delta E_s \qquad (6.1)$$

In this equation $1/r_1 = k_{12}/k_{11}$ represents the reactivity of a vinyl ester relative to the reference monomer, toward a radical chain end which has a reference-monomer ultimate unit; σ^* and E_s are Taft's polar and steric substituent constant, successively; and ρ^* and δ are the respective reaction constants. Figure 6-1 shows linear relationships of $\log\,(1/r_1)$ versus the polar substituent constant σ^* for the various binary combinations.

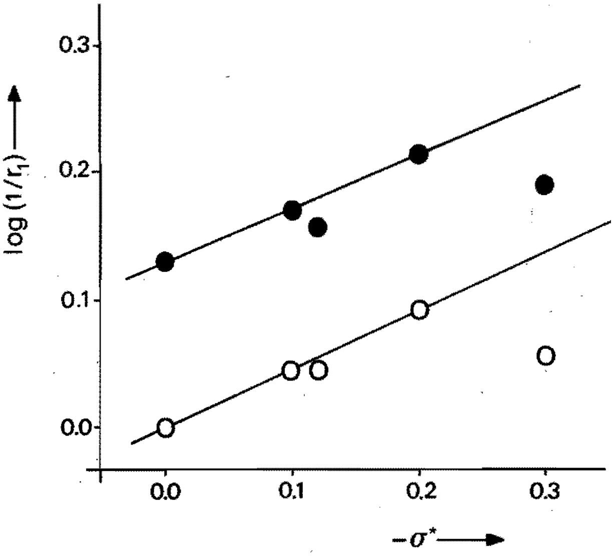


Figure 6-1 Relation between $\log(1/r_1)$ and $-\sigma^*$ for the copolymerizations of the homologous series of vinyl esters with ethylene[8] (●) and with vinyl acetate[11] (o) as reference monomers in *tert*-butyl alcohol at 335 K and 3.4 MPa. $-\sigma^*$: vinyl acetate 0.0; vinyl propionate 0.1; vinyl butyrate 0.12; vinyl isobutyrate 0.2; and vinyl pivalate 0.3.

However, the reactivity of VPV toward both the reference macroradicals is significantly lower than would be expected, considering its polar reaction constant only. Van der Meer et al.[3,8,11] concluded that steric hindrance occurs in those propagation reactions within the system Eth-VAc-VPV involving at least one VPV unit as monomer or macroradical, except for the addition of Eth to a VPV macroradical. These conclusions are summarized in Table 6-3.

Table 6-3 Proposed occurrence of sterically hindered propagations (+) within the system ethylene (Eth)-vinyl acetate (VAc)-vinyl pivalate (VPV)[11].

	Radicals		
Monomers	∿Eth•	∿VAc•	∿VPV•
Eth	-	-	$\overset{?}{-}$
VAc	-	-	+
VPV	+	+	+

effect of solvent[12]

The effect of solvent on vinyl ester reactivity was investigated by means of the Eth-VAc copolymerization in four different solvents, viz., *tert*-butyl alcohol (TBA), isopropyl alcohol (IPA), benzene (Bz), and *N*,*N*-dimethylformamide (DMF). The dependence of the r values on the nature of the solvent was correlated with the volume changes (= excess volumes) observed on mixing VAc with the relevant solvent (Figure 6-2). An increased hydrogen bonding or dipole-dipole interaction through the carbonyl moiety of the ester group of VAc, induces a decreased electron density on the vinyl group, which in turn leads to a decreased VAc reactivity. This fits in well with the results obtained in the investigation of the effect of monomer structure on vinyl ester reactivity, where reactivity appeared to increase with decreasing electron-withdrawing ability of the ester group[8,11].

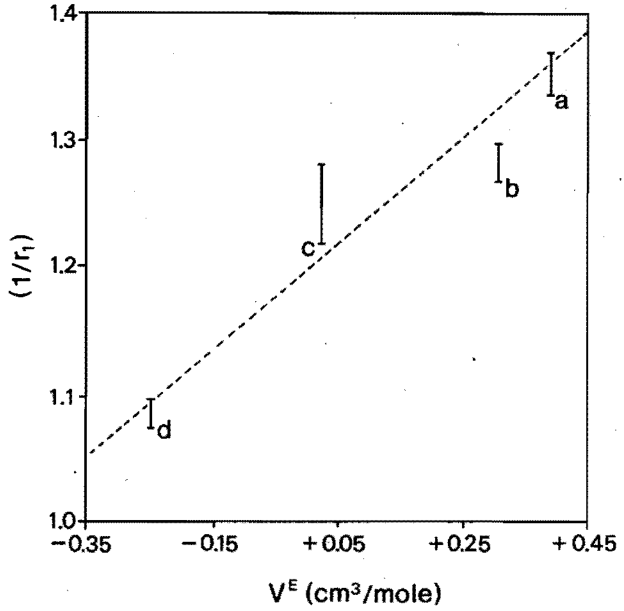


Figure 6-2 $1/r_1$ of ethylene-vinyl acetate at 3.4 MPa and 335 K versus the excess volume V^E (at mole fraction vinyl acetate, $x = 0.1$) for mixtures of vinyl acetate with various solvents[12]: (a) *tert*-butyl alcohol, (b) isopropyl alcohol, (c) benzene, and (d) *N,N*-dimethylformamide.

effect of pressure[3, 9, 10]

The copolymerization of the binary combinations of Eth-VAc-VPV in TBA has been investigated at various pressures up to 118 MPa. As was pointed out in section 4.4.1 the pressure-dependence of the *r* values is governed by differences between the activation volumes for the homopropagation and crosspropagation reactions[3] (Table 6-4). The results were interpreted in terms of the concept of additivity[9] (see also section 4.4.2). This scheme is based on the assumption that the activation volume of a propagation reaction is separable into characteristic contributions of monomer and radical regardless of the combination involved. If this concept is valid the activation volume differences A and B have equal but opposite values:

$$\underbrace{\Delta V_{11}^{\#} - \Delta V_{12}^{\#}}_{A} + \underbrace{\Delta V_{22}^{\#} - \Delta V_{21}^{\#}}_{B} = 0 \qquad (6.2)$$

Table 6-4 Activation volume differences of binary copolymerizations of ethylene (Eth)-vinyl acetate (VAc)-vinyl pivalate (VPV) in *tert*-butyl alcohol (pressure range 3.4-118 MPa)[3].

Monomer combination	$\Delta V_{11}^{\#} - \Delta V_{12}^{\#}$ = A	$\Delta V_{22}^{\#} - \Delta V_{21}^{\#}$ = B
Eth-VAc	-1.9 ± 0.4^{a}	$+2.3 \pm 0.3^{a}$
Eth-VPV	-4.8 ± 0.5	$+4.4 \pm 0.5$
VAc-VPV	$+1.0 \pm 0.1$	$+2.7 \pm 0.3$

[a] Estimated standard deviation.

This was found in Eth-VAc and Eth-VPV but not in VAc-VPV which was attributed to steric hindrance. As a sterically hindered reaction is generally assumed to be more accelerated by pressure than an unhindered one, there will be an additional negative contribution to the relevant activation volume. In Eth-VPV the addition of VPV to both the Eth macroradical and the VPV macroradical was assumed to be sterically hindered (Table 6-3). Provided the additional negative contributions to $\Delta V_{12}^{\#}$ and $\Delta V_{22}^{\#}$ are equal, A + B remains zero and the additivity scheme still holds. In VAc-VPV three propagation reactions are assumed to be sterically hindered. As a result the criterion in eq. 6.2 will not be met.

Since the occurrence of steric hindrance should lower the absolute values of A and B in Eth-VPV, the relatively high values of these differences (Table 6-4) are surprising. This was explained by an increased hydrogen bonding between VPV and TBA as pressure increases, leading to a decreased VPV reactivity[3] (see also effect of solvent). In this way the greater acceleration due to steric hindrance might be compensated by a diminished reactivity of VPV. According to van der Meer[3] the effect of hydrogen bonding holds equally for both VAc and VPV, and may thus not show up significantly in the relevant activation volume differences of the VAc-VPV copolymerization.

Based on the information available at that time, van der Meer et al. have drawn two main conclusions from the above results. First, the reactivity of a vinyl ester should be a function of the electron density on the double bond. Secondly, deviations from this observation can be explained by means of sterically hindered propagation reactions.

However, present research has shown that for a number of reasons, that will be discussed in this chapter, an explanation based on steric hindrance seems unlikely. Evidence is provided which supports the view that the exceptional position of VPV is solvent-dependent, and is only to be found in TBA. Furthermore, we investigated the pressure-effect on the copolymerization of Eth with vinyl propionate (VP). The results are not consistent with the additivity scheme. As a consequence, the earlier explanation was rejected and an alternative model for the effect of pressure on vinyl ester reactivity is developed, which is based on the Hammond postulate.

6.2 Experimental

6.2.1 Materials

The specification of the monomers Eth, VP, and ViB, the radical initiator α,α'-azobisisobutyronitrile (AIBN), and the solvents TBA and DMF have been reported elsewhere[8,12]. Isobutyl alcohol (Merck, p.a.) and methyl alcohol (Merck, p.a.) were used without purification. An improved synthesis has been developed for VPV.

synthesis of vinyl pivalate

A great number of methods are known for the synthesis of vinyl esters[14-20]. Most of these methods are useful in specific cases only, or unsuitable for laboratory scale. An example of the latter is the direct vinylation of carboxylic acid. On the other hand, only VAc, VP and vinyl versatates are produced on a large scale. In case of other vinyl esters, the vinyl interchange method is commonly used. Mostly, excess vinyl acetate (VAc : RCOOH = 6 : 1) is used in the presence of mercuric salts.

$$RCOOH + CH_3COOCH = CH_2 \xrightarrow{HgSO_4} RCOOCH = CH_2 + CH_3COOH$$

There are three major reactions of vinyl acetate with carboxylic acids: (1) the vinyl interchange reaction, which occurs at low temperature (290-350 K) in the liquid phase, (2) the formation of ethylidene diesters at somewhat higher temperatures, and (3) the formation of anhydrides of the acids present, in the vapor phase. If the reaction temperature is kept at 300 K or below high yields of vinyl esters are obtained. However, this method requires long reaction times. Mondal et al.[18] changed the vinylating agent from vinyl acetate to the high-boiling vinyl versatate-10 (VV10). A molar ratio 2 : 1 of VV10 to carboxylic acid is sufficient to drive the reaction to the right by continuous distillation of the vinyl ester formed (reaction time 3-5 hours; yield 20-70%). However, the high bath temperature required (ca. 410 K) probably explains why in case of pivalic acid the vinyl interchange reaction becomes a side reaction (yield ca. 10%). Following Irvin and McGrail[20], we used the method of Mondal et al. at reduced pressure (75 mm Hg). In this way the bath temperature is kept below 350 K. Vinyl pivalate was obtained in high yield (ca. 80%) and had the following physical constants: b.p. 325 K/75 mm, $n_D^{20} = 1.4059$, $d_4^{20} = 0.870$, $d_4^{62} = 0.824$.

6.2.2 Copolymerization

All free-radical copolymerizations were carried out at 335 K. The Eth-VP copolymerization at 59 MPa in TBA was investigated by means of the "quenching" method[10] (see also chapter 5). The copolymerization of Eth with VPV in DMF at 3.4 MPa was investigated by means of the "sequential sampling" method[4] (see also chapter 5). The experimental conditions are summarized in the Tables 6-5 and 6-6. The monomer feed composition was determined by means of quantitative GLC. The GLC conditions for Eth-VP-TBA are identical to those reported elsewhere[8].

Table 6-5 Experimental conditions of the copolymerization of ethylene (M_1) with vinyl propionate (M_2) in *tert*-butyl alcohol at 59 MPa and 335 K with the "quenching" method.

Number of GLC observations during the initial stage	Average initial monomer feed ratio	Number of GLC observations during the final stage	Average final monomer feed ratio	Average degree of conversion based on M_2 (%)	Total initial monomer concentration (mole/dm^3)	Initiator concentration (mmole/dm^3)
17	3.574	11	3.667	8.0	1.1	5.1
11	2.807	13	2.938	14.0	1.6	5.6
13	2.092	9	2.211	16.9	0.9	5.1
9	1.789	11	1.900	18.2	0.8	6.1
14	1.299	13	1.360	14.6	0.8	5.1
11	1.070	9	1.175	27.4	1.1	5.1
13	1.017	14	1.052	11.3	0.7	5.1
14	0.973	10	1.013	12.9	0.9	5.6
12	0.937	10	1.025	26.6	0.9	5.1
10	0.904	10	1.015	32.8	1.5	5.6
11	0.819	12	0.889	24.5	1.5	5.6
13	0.784	12	0.847	24.8	1.5	5.6
16	0.759	15	0.812	21.1	1.1	5.1
11	0.611	7	0.669	27.7	1.3	5.6
14	0.541	12	0.596	28.7	1.5	5.6
16	0.494	10	0.557	34.8	1.0	5.6

Table 6-6 Experimental conditions of the copolymerization of ethylene (M_1) with vinyl pivalate (M_2) in *N*,*N*-dimethylformamide at 3.4 MPa and 335 K with the "sequential sampling" method.

Initial monomer feed ratio q_0	Final monomer feed ratio	Conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mole/dm^3)	Initiator concentration (mmole/dm^3)
2.530	2.633	16.3	19	Varying from 0.9 to 1.8	Approximate 0.4
2.017	2.104	17.4	16		
1.438	1.512	20.9	22		
1.191	1.249	20.0	18		
0.990	1.046	23.5	19		
0.789	0.827	21.0	21		
0.549	0.581	25.3	16		
0.247	0.261	25.4	14		

For Eth-VPV-DMF: column temperature 397 ± 0.1 K; stationary phase: 15% by wt Carbowax 6000 based on Chromosorb PAW, mesh 60-80 (Johns Manville).

The r values have been determined by means of the improved curve-fitting I procedure[13].

6.2.3 Density measurements

Density measurements have been carried out by means of a vibrating-tube densimeter, i.e., a Paar Precision Density Meter, model DMA 10. The equation for the derivation of the excess volumes from the densities of the binary mixtures is given elsewhere[12].

6.3 Results and discussion

An important conclusion from the investigation of the effect of solvent on the reactivity of VAc[12] was that increased hydrogen bonding with solvent decreases VAc reactivity. The same argument, viz., the reactivity of a vinyl ester decreases with pressure due to increased hydrogen bonding, was used to explain the relatively large activation volume differences A and B observed for Eth-VPV[3] (Table 6-4). This effect was assumed to compensate the greater acceleration due to pressure of the addition of VPV to the Eth macroradical and to the VPV macroradical due to steric hindrance. Furthermore, it was stated that the argument of hydrogen bonding holds equally well for both VAc and VPV. However, the addition of VAc to the Eth macroradical was assumed not to be sterically hindered. Therefore, while $\Delta V_{11}^{\#} - \Delta V_{12}^{\#}$ (= A) for Eth-VPV would contain an additional negative contribution to $\Delta V_{12}^{\#}$, arising from steric hindrance, there should not be a similar contribution to A for Eth-VAc. This leads to the expectation that $|A|$ for Eth-VPV should be equal to or less than $|A|$ for Eth-VAc. The experimental results (Table 6-4) do not confirm the prediction, and the interpretation in terms of sterically hindered additions is thus questionable. Again, in the copolymerization of the homologous series of vinyl esters with Eth as reference monomer (Table 6-2), only the value of r_1 for Eth-VPV is significantly deviant, whereas both the addition of VPV to the Eth macroradical (expressed in r_1) and to the VPV macroradical (expressed in r_2) should be sterically hindered. Furthermore, according to Jenkins[21] all treatments of reactivity which attribute differences in reactivity to activation energy differentials are very succesful on the assumption that steric hindrance is negligible in monomers substituted on only one side of the double bond. Moreover, alkoxy groups (RO-) have comparatively small steric hindering effects because of the bond angle and flexible nature of the C-O-C linkage[22].

An alternative explanation of the exceptional position of VPV in the homologous series of vinyl esters may be found in the role of the solvent. Van der Meer et al.[12] successfully correlated the effect of solvent on the Eth-VAc copolymerization with the measured volume

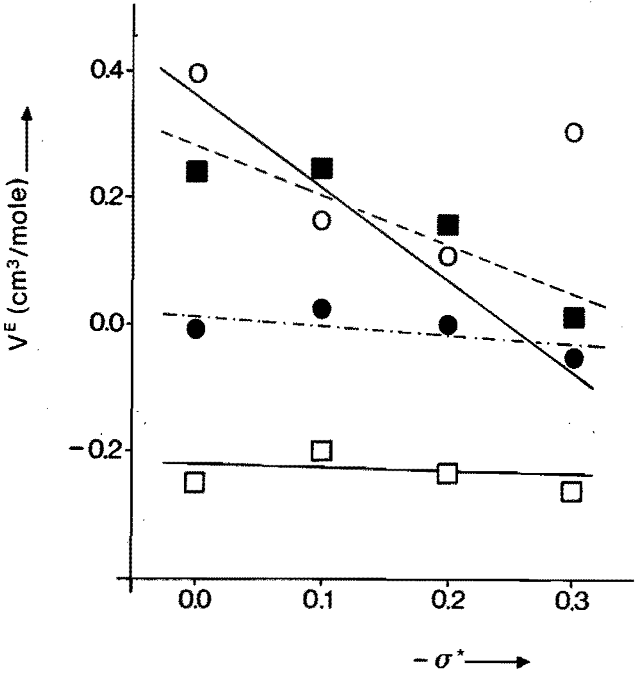


Figure 6-3 The excess volume V^E versus $-\sigma^*$ for vinyl acetate (0.0), vinyl propionate (0.1), vinyl isobutyrate (0.2), and vinyl pivalate (0.3) in various solvents: (o) *tert*-butyl alcohol, (■) isobutyl alcohol, (●) methyl alcohol, and (□) *N,N*-dimethylformamide (at mole fraction vinyl ester, x = 0.1).

changes (= excess volumes) observed on mixing VAc with the various solvents (Figure 6-2). Their results were reexamined and extended to the excess volumes obtained on varying vinyl esters as well as solvents. The excess volume V^E is dependent on both the monomer-solvent combination involved and the composition of the binary mixture. Therefore, in the subsequent discussion the excess volumes observed at mole fraction vinyl ester of 0.1 (T = 335 K, P = 0.1 MPa) are used. This mole fraction corresponds approximately with the average molar concentration of the vinyl esters in the copolymerization reaction mixture. In Figure 6-3 the excess volume V^E in various solvents has been plotted versus the Taft polar substituent constant of the vinyl esters. In Figure 6-4 $1/r_1$ has been plotted versus V^E in TBA.

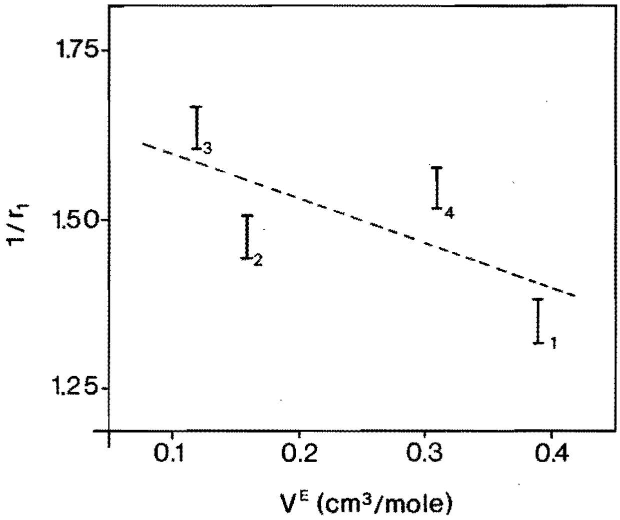


Figure 6-4 $1/r_1$ for ethylene-vinyl ester copolymerizations in *tert*-butyl alcohol versus the excess volume V^E (at mole fraction vinyl ester, $x = 0.1$) for mixtures of *tert*-butyl alcohol with the various vinyl esters: (1) vinyl acetate, (2) vinyl propionate, (3) vinyl isobutyrate, and (4) vinyl pivalate.

According to van der Meer et al.[12] the excess volumes are characteristic of specific interactions closely connected with the cause of the solvent-dependent variations of VAc reactivity. Together with the Figures 6-3 and 6-4 this indicates that the exceptional position of VPV in the homologous series of vinyl esters is solvent-dependent and is only found in reactions for which TBA is used as solvent. This explanation is furthermore supported by a comparison of the r values of the Eth-VAc and the Eth-VPV copolymerization in DMF.

$$\left.\begin{aligned} r_1 &= 0.92 \pm 0.01 \\ r_2 &= 1.04 \pm 0.02 \end{aligned}\right\} \quad \text{Eth-VAc-DMF}^{12}$$

$$\left.\begin{aligned} r_1 &= 0.75 \pm 0.01 \\ r_2 &= 1.20 \pm 0.02 \end{aligned}\right\} \quad \text{Eth-VPV-DMF}$$

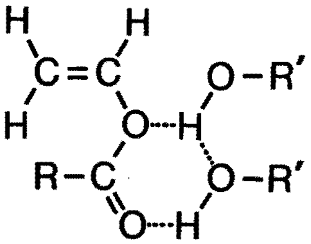
Two important conclusions may be drawn from these r values. First, the excess volume V^E in DMF is the same for all vinyl esters (Figure 6-3). In combination with Figure 6-4 this leads to the expectation that the r_1 values will be equal in all vinyl ester copolymerizations with Eth as reference monomer and DMF as solvent. However, as can be seen from the above figures the r_1 values of Eth-VAc and Eth-VPV differ significantly. This indicates that in case of DMF as solvent vinyl ester reactivity is not correlated with the excess volume. The good fit of DMF in Figure 6-2 is, therefore, probably coincidental. Secondly, as already pointed out $1/r_1$ represents the reactivity of a vinyl ester relative to the reference monomer, toward the reference macroradical. The relative reactivity of VPV and VAc toward the Eth macroradical in both DMF and TBA is given by:

$$\frac{1/r_1\ (\text{VPV})}{1/r_1\ (\text{VAc})} = \frac{r_1\ (\text{VAc})}{r_1\ (\text{VPV})} \qquad \begin{aligned} &\text{DMF} : 1.26 \\ &\text{TBA} : 1.16 \end{aligned}$$

These ratios indicate that with DMF as solvent, VPV constitutes no exception in the copolymerization of the homologous series of vinyl esters with Eth as reference monomer.

An interesting conclusion may be drawn from Figure 6-3. On mixing the vinyl esters with alcohols of increasing acidity both the magnitude of the excess volumes and the slopes of V^E versus $-\sigma^*$ decrease. Increased hydrogen bonding between vinyl ester and alcohol enhances the electron-withdrawing character of the entire ester side group and could make the difference in vinyl ester reactivity on varying the alkyl group less pronounced. On the strength of this argument we predict that, with methyl alcohol as solvent, no difference in vinyl ester reactivity will be observed, and verification of this would be very interesting.

Figure 6-2 and 6-4 shown opposite signs for the relations between V^E and reactivity ($1/r_1$). This apparent contradiction, observed when varying the alkyl groups in the vinyl ester (R) and in the alcohol (R'), can now be explained satisfactorily. It is remarked that the structure given below represents only one of many, possibly occurring vinyl ester-alcohol interactions.



R : $CH_3 \rightarrow C(CH_3)_3$	decreasing electron-withdrawing character of the ester side group; enhanced electron density on double bond; increasing electronegativity on the carbonyl O atom; decreasing excess volumes $\rightarrow V^E$ decreases as $1/r_1$ increases.
R' : $CH_3 \rightarrow C(CH_3)_3$	decreasing acidity of the alcohol; enhanced excess volumes; decreasing electron-withdrawing character of the ester side group; enhanced electron density on the double bond $\rightarrow V^E$ increases as $1/r_1$ increases.

The food fit of VPV in Figure 6-4 is probably by coincidence, because a greater excess volume is found in combination with a lower VPV reactivity when compared with the other vinyl ester-alcohol combinations. The lower reactivity points to a diminished electron density on the double bond, which may be due to an improved packing in the liquid phase leading to interaction with an additional TBA molecule. On the other hand, this should lower the expected excess volume, because hydrogen bond formation almost always results in a volume contraction. However, due to the fact that VPV as well as TBA possess a *tert*-butyl group these hydrogen bonds may have a preferential direction leading to a more positive excess volume. An elegant example of this phenomenon is the greater volume of ice as compared to water. However, the detailed physical background of the observed VPV reactivity in TBA remains unexplained.

To a good approximation the additivity scheme is experimentally established as valid for both Eth-VAc and Eth-VPV, but not for VAc-VPV[3]. Its failure in the latter case was given an explanation in terms of steric hindrance, which in turn required a re-interpretation, in terms of steric hindrance, of its validity for Eth-VPV. However, the V^E data indicate that the results may be better explained by a certain type of interaction between VPV and TBA not found in other vinyl ester-alcohol combinations. In order to obtain additional evidence the copolymerization of Eth with VP in TBA was investigated at various pressures.

Table 6-7 Monomer reactivity ratios for the copolymerization of ethylene (M_1) with vinyl propionate (M_2) in *tert*-butyl alcohol at different pressures, and pertaining activation volume differences.

Pressure (MPa)	r_1	r_2	$\Delta V_{11}^{\#} - \Delta V_{12}^{\#} = A$	$\Delta V_{22}^{\#} - \Delta V_{21}^{\#} = B$
3.4[a]	0.67 ± 0.01	1.50 ± 0.01	0 ± 0.3[c]	4.0 ± 0.3[c]
59	0.68 ± 0.01	1.37 ± 0.02		
118[b]	0.67 ± 0.01	1.28 ± 0.01		

[a] Ref. 8

[b] Chapter 5 of this thesis

[c] Estimated standard deviations

The results are given in Table 6-7 together with the pertaining activation volume differences. As eq. 6.1 is not fulfilled it can be concluded that in the case of Eth-VP, the additivity scheme cannot be used to explain the observed pressure-effect.

Instead of the additivity scheme, the concept based on the *Q-e* scheme can be used for the interpretation of the observed pressure-effect[23,24]. Jenner gives *Q-e* values for Eth, VAc, and VPV at 0.1 MPa and 300 MPa, permitting the calculation of *r* values at both pressures and from that the direction of the pressure-effect (see also sections 4.4.2 and 4.4.3). As can be seen from Table 7-8 the calculated *r* values at 0.1 MPa deviate strongly from the experimental values, except for Eth-VPV.

Table 6-8 Monomer reactivity ratios at 0.1 MPa and 300 MPa calculated by means of the concept based on the *Q-e* scheme[23,24].

Monomer combination		*r* values	
		0.1 MPa[a]	300 MPa
Eth-VAc	r_1	0.248 (0.74)	0.993
	r_2	4.040 (1.50)	1.122
Eth-VPV	r_1	0.648 (0.64)	1.087
	r_2	1.545 (1.49)	0.920
VAc-VPV	r_1	2.614 (0.88)	1.220
	r_2	0.383 (1.17)	0.914

[a] Values in parenthesis are the *r* values observed at 3.4 MPa (see Table 6-2).

However, this may not be surprising, since Jenner probably calculated the *Q-e* values for VPV from the *r* values given by van der Meer and German[25]. In our opinion a consideration of the effect of pressure on *r* values by means of the concept based on the *Q-e* scheme is meaningless.

Neither the concept of additivity nor the concept based on the *Q-e* scheme take into account the reactivity of the macroradical. In our opinion a reliable description of reactivity and the pressure-effect on reactivity in free radical copolymerization should take into account contributions, which depend on the structure of both monomer and radical (see also section 2.4). Therefore we developed a new approach based on the Hammond postulate as used by Asano and Le Noble[26] (see also section 4.4). In this concept decreasing reactivity is directly related to a more negative activation volume because the pertaining activated complex becomes more product-like. The applicability of the Hammond postulate in the explanation of the effect of pressure on *r* values will be discussed by means of the binary copolymerization of Eth with VAc, VP and VPV (Table 6-9).

Table 6-9 Activation volume differences for ethylene (M_1)-vinyl ester (M_2) copolymerizations in *tert*-butyl alcohol (pressure range: 3.4-118 MPa).

Monomer combination	$\Delta V_{11}^{\#} - \Delta V_{12}^{\#} = A$	$\Delta V_{22}^{\#} - \Delta V_{21}^{\#} = B$
Eth-VAc[a]	-1.9 ± 0.4[b]	2.3 ± 0.3[b]
Eth-VP	0 ± 0.3	4.0 ± 0.3
Eth-VPV[a]	-4.8 ± 0.5	4.4 ± 0.3

[a] Ref. 3

[b] Estimated standard deviations

The effect of pressure on *r* values is governed by differences between activation volumes. According to the Hammond postulate the activation volume of the homopropagation reaction should differ from that of the crosspropagation reaction due to the difference in reactivity of Eth and the vinyl ester toward, for example, the vinyl ester macroradical. As the difference in reactivity is increased, the value of B will also increase (Figure 6.5). It has been shown that measured by the r_2 value VPV is not an exception. Therefore, the effect of pressure on the r_2 value in the copolymerization of a homologous series of vinyl esters shows, according to the Hammond postulate, that the reactivities of vinyl esters with respect to the ethylene monomer increase in the order VAc < VP < VPV, which is reflected in the value of the differences B (Table 6-9). In the same line of argument the effect of pressure on r_1 can be discussed.

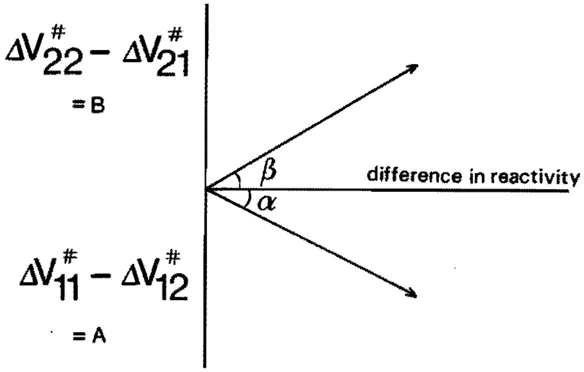


Figure 6-5 Schematic representation of the directional correlation between activation volume differences and reactivity differences, according to the Hammond postulate ($\alpha \neq \beta$) and the additivity scheme ($\alpha = \beta$).

If there were no effect of radical reactivity the absolute values of the differences A and B would be equal for each monomer combination, a situation which is found in the concept of additivity (Figure 6-5). However, the new data for Eth-VP clearly shows that this situation is not met in practice. Normally, the more reactive the radical, the less the difference in activation volume (= reactivity) experimentally observed. As the ethylene radical is more reactive than a vinyl ester radical, the absolute magnitude of A should be less than the absolute magnitude of B, a situation which is certainly the case for VP, very probably true for VAc, but does not hold for VPV. However, it should be remembered that r_1 of Eth-VPV is an exception due to a deviating interaction with the solvent TBA, for which there is independent experimental evidence. Therefore, it is concluded that the effect of pressure on the reactivity of a homologous series of vinyl esters in the copolymerization with Eth as reference monomer is in good agreement with the Hammond postulate. There is also evidence that an abnormal specific interaction between ester and solvent can introduce a perturbing effect within the general pattern of reactivity.

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Chapter 7

Relations between Structure and Reactivity of a Series of Conjugated Monomers; Comparison with Unconjugated Monomers

Synopsis

The copolymerization behavior of conjugated monomers, as reported in the literature, differ greatly from the results obtained in the case of unconjugated vinyl esters. A thorough investigation of the copolymerization behavior of the former type of monomers and a comparison between conjugated and unconjugated monomers may, therefore, yield additional information. This chapter describes the copolymerization of methyl vinyl ketone (MVK), methyl acrylate (MA), and methyl methacrylate (MMA) with styrene (St) as reference monomer at 3.4 MPa and 335 K with toluene as solvent. In addition, the effect of pressure on the binary copolymerizations of St-MA-MMA is discussed. It appears that in case of conjugated monomers reactivity decreases as the electron-donating character of the substituents increases, whereas the reverse is found in unconjugated monomers. This is explained by the findings that in conjugated monomers resonance effects induced by polar factors play a dominant role, whereas in unconjugated monomers mainly polar factors are governing the relative reactivities. The r *values at 3.4 MPa are compared with those predicted by means of the* Q-e *scheme and* Patterns. *No definite conclusions could be drawn about the applicability and validity of either scheme, although* Patterns *shows excellent result in case of the* H *function of Mayo. In vinyl ester copolymerizations and Le Noble and Asano's example of the Menshutkin reaction one single factor (polarity and steric hindrance, successively)*

dominates $\Delta G^{\#}$, ΔG, and $\Delta V^{\#}$. This allows of a straightforward interpretation of the results with the Hammond postulate and is in full agreement with Evans's potential energy calculations. In conjugated monomers, however, an interplay of resonance and *polar factors is found. The general validity of these findings need further experimental and theoretical support. The overall activation volume expressing the effect of pressure on the number-average degree of polymerization in St-MMA varies from -19 ± 3 cm^3/mole to -24 ± 2 cm^3/mole upon variation of the mole fraction St from 0 to 1 and fits in very well with the literature value of -20 cm^3/mole for St.*

7.1 Preface

In the previous chapter the effect of monomer structure, pressure, and solvent on the reactivity of a homologous series of vinyl esters has been discussed. However, the results of this investigation raise new questions concerning the effects of these variables on the reactivity of various types of vinyl monomers and corresponding radicals. Vinyl monomers can be roughly divided into two classes: reactive (conjugated) monomers and unreactive (unconjugated) monomers. In this context, conjugated monomers are those monomers in which the double bond of the vinyl group is conjugated with another multiple bond, whereas in unconjugated monomers this type of conjugation is not present. Conjugated monomers exhibit a strong tendency to add to any radical chain end, because the resulting radical is strongly stabilized by resonance. Unconjugated monomers, on the other hand, exhibit a weaker tendency to add to any given radical, because in this case the resulting radical is much less stabilized by resonance. These arguments are graphically shown in a representation[1] of Evans's calculations[2,3] for systems dominated by resonance factors (Figure 7-1). The resonance stabilization of a monomer (if any) has been taken as half that of the resulting radical.

The differences in copolymerization behavior between conjugated monomers (i.e. unreactive radical and reactive monomer) and unconjugated monomers (i.e. reactive radical and unreactive monomer) find expression in various ways:

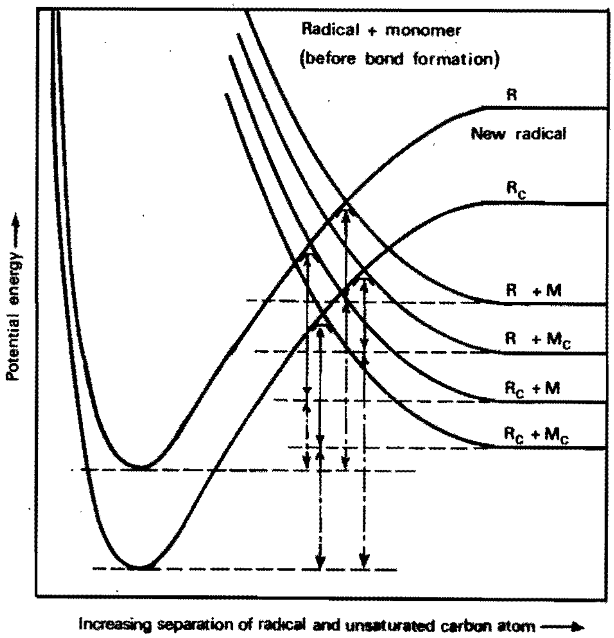

Figure 7-1 Potential energy of system, monomer plus radical, as a function of separation of radical and unsaturated carbon atom. Subscript c indicates conjugation in monomer (M) or radical (R). Arrows with solid lines indicate energies of activation; broken lines heats of reaction[1].

- In case of vinyl esters (unconjugated monomers) reactivity appears to increase as the electron-donating character of the substituents increases (chapter 6), whereas the reverse is found in conjugated monomers[4-9].
- Asai and Imoto[10] observed different pressure-effects between systems with two conjugated monomers and binary systems in which one of the monomers is unconjugated.
- The variation in *r* values with solvent is dependent on the nature of both monomer and corresponding radical. However, the effect of a substituent on reactivity is much greater at a radical than at a monomer. For example, the styrene macroradical is about 1000 times less reactive than the vinyl acetate radical toward a given monomer (if polar effects are of minor importance), but styrene monomer is only about 50 times more reactive than vinyl acetate monomer toward

a given radical. Therefore, the extent to which a monomer and the corresponding radical, and through this the *r* values, are affected by the solvent will be different in conjugated and unconjugated monomers.

These observations are sufficient motives to call for the investigation of a series of conjugated monomers. In addition the comparison of the results with those obtained from the investigation of unconjugated monomers will be of the utmost importance. The actual choice of the monomers was chiefly determined by the following requirements. Variation in substituents should result in a significant change in monomer reactivity, but the monomers should not be too different in reactivity in order to allow a reliable determination of *r* values.

As a consequence, in the present investigation monomers possessing a C = C - C = O group, viz., (meth)acrylates and vinyl ketones were chosen.

7.2 Introduction

The free-radical copolymerization of styrene (St) with methyl methacrylate (MMA) at normal pressure has been the subject of more scientific research and publications than any other monomer pair. In 1944 Mayo and Lewis[11] used this copolymerization to illustrate their derivation of the Alfrey Mayo model. Later on, many investigators used this monomer pair to support new experimental techniques or (improved) calculation procedures for *r* values. This led to *r* values for St-MMA failing to show mutual agreement[12]. The discrepancies among *r* values far beyond the experimental errors should serve as a warning against the casual acceptance of any single set of data. Furthermore, this points to the need for a scrutiny of the calculation procedures.

A great number of (meth)acrylates and vinyl ketones have been investigated by means of the copolymerization with a reference monomer[4-9,13]. The relative reactivities toward the reference macroradical are described by the Taft relation (eq. 7.1, see also chapter 6) and a modified Hammett equation derived by Yamamoto et al.[5,14] (eq. 7.2):

$$\log \text{(rel. react.)} = \rho^* \sigma^* + \delta E_S \quad (7.1)$$

$$\log \text{(rel. react.)} = \rho \sigma + \gamma E_R \quad (7.2)$$

In eq. 7.2 σ is Hammett's polar substituent constant, E_R is the resonance substituent constant and ρ and γ are reaction constants. The results are summarized in Table 7-1. In most cases (1-5) the relative reactivities of these monomers toward the reference macroradical appears to be influenced exclusively by polar factors ($\delta = 0$). In case of *p*-substituted phenyl vinyl ketones (7) and nuclear substituted phenyl methacrylates (8) both polar and resonance effects are important in the explanation of the relative reactivities. In α-alkyl acrylates (6) it is obvious that steric hindrance plays an important role, since the alkyl group is attached directly to the reacting vinyl site.

Table 7-1 Copolymerization of series of (meth)acrylates and vinyl ketones with various reference monomers.

	Type of series of monomers	Reference monomer	ρ^*	δ	ρ	γ	Reference
1	methacrylates	styrene	0.33	0			6
2	methacrylates	β-chloroethyl methacrylate	0.13	0			6
3	methacrylates	methyl methacrylate	∿0.2	0			7
4	acrylates	styrene	0.56	0			5
5	vinyl ketones	styrene	0.40	0			9
6	α-alkyl acrylates	styrene	0	∿0.6			13
7	p-substituted phenyl vinyl ketones	styrene			0.34	2.0	9
8	nuclear-substituted phenyl methacrylates	styrene			0.21	1.0	5

The results obtained in the investigations of the solvent-effect on copolymerizations involving acrylates and vinyl ketones are diverse and inconsistent[9,15-18]. On increasing the polarity of the solvents, the *r* values may go in either direction. The apparent discrepancies between the results of these investigations may be partly due to an unreliable determination of *r* values. In addition, a detailed interpretation of the solvent-effect is hampered by the fact that the solvent affects the reactivity of the two monomers and the two radicals at the same time. As a consequence, the overall-result may vary with the solvent.

A number of copolymerizations involving (meth)acrylates and vinyl ketones have been investigated under pressure[10,19-26]. In chapter 4 three models were described for the explanation of the pressure-effect on reactivity in free-radical copolymerization. However, it is very difficult to discriminate between these models in the case of conjugated monomers. This may be due to an unreliable determination of r values, the great number of monomer-solvent interactions possible and the differences in pressure-sensitivity of these interactions.

From the foregoing it may be concluded that the insufficient and even contradictory information found in the literature, justifies a thorough investigation of reactivity and relations between structure and reactivity in conjugated monomers. This chapter describes the investigation of copolymerizations of methyl vinyl ketone (MVK, $CH_2 = CH - COCH_3$), methyl acrylate (MA, $CH_2 = CH - COOCH_3$), and methyl methacrylate (MMA, $CH_2 = C(CH_3) - COOCH_3$) with styrene (St) as reference monomer at 3.4 MPa and 335 K with toluene as solvent. In addition, the effect of pressure on the binary copolymerizations of St-MA-MMA and on the number-average degree of polymerization ($\overline{P}_n$) for St-MMA are discussed. Furthermore, the relations between reactivity and monomer structure are discussed and compared with those found in the homologous series of unconjugated monomers, viz., vinyl esters (chapter 6).

7.3 Experimental

7.3.1 Materials

The monomers styrene (Fluka), methyl vinyl ketone (Merck), methyl acrylate (BDH, Ltd.), and methyl methacrylate (Fluka) were distilled at reduced pressure in a nitrogen atmosphere. The middle fraction of the distillate was collected and used. In all cases the distillate was found to be > 99.5% pure by GLC analysis. The free-radical initiator α,α'-azobisisobutyronitrile (Fluka, p.a.) and the solvent toluene (Merck, p.a.) were used without purification.

7.3.2 Copolymerization

At all relevant pressure levels the free-radical copolymerizations were carried out at 335 K by means of the "sequential sampling" method (see chapter 5) using toluene as solvent. The monomer feed composition was determined by means of quantitative GLC. The GLC conditions were: stationary phase, 10-15% by wt of squalane on chromosorb W AW DMCS 80-100 mesh (Johns Manville); column length and temperature (between 360 K and 380 K) depending on the binary combination involved; detector temperature, 423 K. The experimental conditions are summarized in the Tables 7-2 to 7-5.

The copolymers were isolated and purified by pouring out in methanol, dissolving in chloroform and reprecipitation in methanol. Purified copolymer was dried under vacuum at a temperature of 313 K until no further weight loss was observed.

The *r* values have been evaluated by means of the improved curve-fitting I procedure[27] and the linear regression method[28] (see also chapter 3).

Table 7-2 Experimental conditions of the copolymerization of styrene (M_1) with methyl vinyl ketone (M_2) in toluene at 3.4 MPa and 335 K with the "sequential sampling" method.

Initial monomer feed ratio q_0	Final monomer feed ratio	Conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mole/dm^3)	Initiator concentration (mmole/dm^3)
3.696	3.920	21.4	30	1.0	6.5
2.573	2.671	21.7	25	1.0	6.5
2.057	2.088	17.2	22	1.0	12.2
1.428	1.401	21.8	29	1.1	6.5
1.178	1.119	24.5	26	1.0	12.2
0.975	0.915	19.4	29	1.0	6.5
0.897	0.824	21.2	28	1.0	8.1
0.679	0.596	20.4	30	1.0	8.1
0.589	0.546	10.9	15	1.0	6.5
0.483	0.390	21.4	25	1.0	8.1
0.377	0.283	22.1	27	1.2	8.1
0.289	0.196	23.3	28	1.0	8.1

Table 7-3 Experimental conditions of the copolymerization of styrene (M_1) with methyl acrylate (M_2) in toluene at various pressures and 335 K with the "sequential sampling" method.

Initial monomer feed ratio q_o	Final monomer feed ratio	Conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mole/dm^3)	Initiator concentration (mmole/dm^3)
3.4 MPa					
4.357	4.194	9.2	21	1.0	8.1
3.815	3.589	13.3	19	1.0	8.9
2.959	2.791	11.2	19	1.0	8.1
2.667	2.511	10.8	19	1.0	8.1
1.537	1.395	11.9	19	1.0	8.1
0.872	0.768	10.2	21	1.0	8.1
0.804	0.730	7.5	14	1.0	8.1
0.675	0.574	10.5	25	1.0	8.1
0.506	0.400	11.9	26	1.0	8.1
0.369	0.291	9.7	22	1.0	8.1
0.229	0.144	12.5	27	1.0	8.1
59 MPa					
4.581	4.314	15.8	20	1.0	3.2
3.152	2.943	14.6	21	1.0	4.1
2.537	2.371	12.7	20	1.0	4.1
2.047	1.900	12.1	18	1.0	4.1
1.570	1.407	14.4	22	1.0	4.1
0.965	0.882	8.6	17	1.0	3.2
0.798	0.694	11.2	20	1.0	3.2
0.484	0.394	11.1	18	1.0	4.1
0.280	0.206	10.9	19	1.0	3.2
0.195	0.118	13.5	20	1.0	4.1
118 MPa					
4.288	4.080	15.1	22	1.0	2.4
3.781	3.609	13.2	20	1.0	2.4
3.132	2.970	13.3	22	1.0	2.4
2.662	2.489	14.7	22	1.0	2.4
1.487	1.358	12.9	19	1.0	2.4
0.983	0.859	13.6	19	1.0	2.4
0.596	0.473	15.3	21	1.0	2.4
0.476	0.396	10.7	20	1.0	2.4
0.384	0.283	14.4	23	1.0	2.4
0.199	0.134	12.4	21	1.0	2.4

Table 7-4 Experimental conditions of the copolymerization of styrene (M_1) with methyl methacrylate (M_2) in toluene at various pressures and 335 K with the "sequential sampling" method.

Initial monomer feed ratio q_0	Final monomer feed ratio	Conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mole/dm^3)	Initiator concentration (mmole/dm^3)
3.4 MPa					
5.192	5.222	15.2	23	1.0	8.1
4.545	4.558	15.2	25	1.0	8.1
3.288	3.270	15.3	25	1.0	8.1
2.817	2.794	12.9	22	1.0	8.1
2.373	2.333	15.9	23	1.0	8.1
1.781	1.746	11.1	20	1.0	8.1
1.390	1.358	9.1	16	1.0	8.1
0.778	0.720	15.0	25	1.0	8.1
0.389	0.340	15.3	24	1.0	8.1
59 MPa					
4.593	4.615	10.8	19	1.0	5.7
3.230	3.225	16.4	23	1.0	6.0
1.992	1.948	18.3	26	1.0	5.7
1.295	1.249	14.4	26	1.0	5.7
0.981	0.932	14.5	27	1.0	4.1
0.903	0.843	17.2	21	1.0	5.8
0.806	0.747	16.9	30	1.0	5.7
0.604	0.566	14.6	23	1.0	4.1
0.397	0.344	17.7	25	1.0	4.1
0.185	0.151	17.2	20	1.0	5.7
118 MPa					
3.991	4.056	18.0	24	1.0	4.1
3.627	3.696	24.2	25	1.0	6.5
3.443	3.490	20.6	24	1.0	4.1
2.578	2.582	23.8	24	1.0	6.5
1.624	1.585	20.5	28	1.0	4.1
1.538	1.491	22.5	21	1.0	7.3
1.214	1.166	18.8	21	1.0	4.1
0.756	0.686	22.8	19	1.0	4.1
0.309	0.251	23.6	19	1.0	4.1
0.168	0.113	32.1	18	1.0	7.3

Table 7-5 Experimental conditions of the copolymerization of methyl methacrylate (M_1) with methyl acrylate (M_2) in toluene at various pressures and 335 K with the "sequential sampling" method.

Initial monomer feed ratio q_o	Final monomer feed ratio	Conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mole/dm^3)	Initiator concentration (mmole/dm^3)
3.4 MPa					
3.943	2.961	17.0	22	1.0	3.2
3.618	2.877	13.9	17	1.0	2.8
3.156	2.421	15.8	21	1.0	2.8
2.501	1.865	17.1	23	1.0	3.2
2.007	1.505	16.7	24	1.0	2.8
1.568	1.189	15.9	26	1.0	2.4
1.195	0.920	14.8	20	1.0	2.4
0.934	0.578	25.0	20	1.0	8.1
0.636	0.395	24.1	22	1.0	3.2
0.503	0.324	22.0	22	1.0	2.4
0.377	0.184	32.4	21	1.0	4.9
0.141	0.054	38.4	24	1.0	2.8
59 MPa					
5.024	3.716	18.6	22	1.0	1.2
3.770	3.203	10.5	17	1.0	1.2
3.136	2.263	19.6	23	1.0	1.6
2.024	1.542	16.3	23	1.0	1.2
1.475	1.163	14.1	17	1.0	1.2
1.233	0.707	29.2	24	1.0	2.0
0.617	0.379	24.7	23	1.0	1.2
0.394	0.228	26.0	20	1.0	1.2
0.302	0.123	37.5	21	1.0	1.6
118 MPa					
3.459	2.557	18.5	19	1.0	0.8
2.447	1.676	22.1	22	1.0	0.8
1.908	1.626	9.9	15	1.0	0.8
1.776	1.220	21.4	21	0.7	0.8
1.157	0.737	24.2	21	1.0	0.8
0.984	0.593	26.2	23	1.0	0.8
0.797	0.444	28.9	21	1.0	0.8
0.469	0.186	38.9	20	1.0	1.2
0.408	0.172	36.3	20	1.0	0.8
0.295	0.125	35.2	20	1.3	0.8

7.3.3 Molecular mass

The number-average molecular mass ($\overline{M}_n$) of St-MMA copolymer samples formed at the three pressure levels was determined using a Hewlett Packard High Speed Membrane Osmometer, model 502. Toluene was used as solvent.

7.4 Results

The *r* values of the binary copolymerizations of St-MA-MMA at various pressures and 335 K in toluene are given in Table 7-6. As can be seen from this Table, the results obtained by means of the improved curve-fitting I method[27] and the linear regression method[28] are the same within experimental error, proving the applicability of the latter method. The 95% confidence regions are given in Figure 7-2.

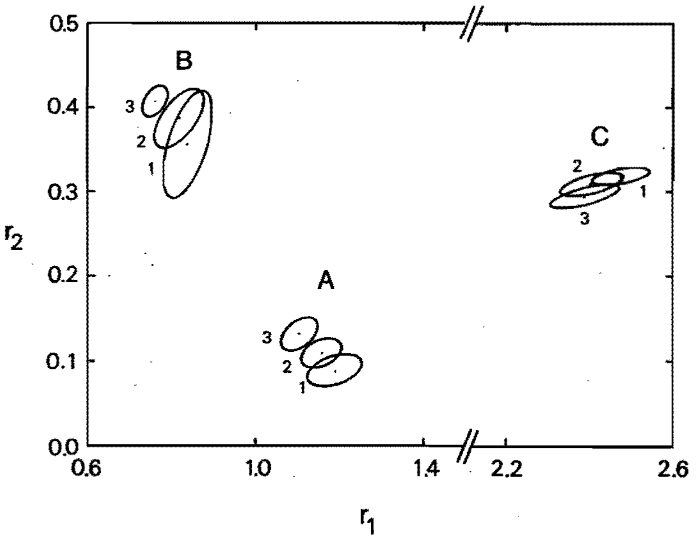

Figure 7-2 The 95% confidence regions for the copolymerizations of: styrene-methylacrylate (A); styrene-methyl methacrylate (B); and methyl methacrylate-methylacrylate (C), at various pressures: 3.4 (1), 59 (2), and 118 (3) MPa.

Table 7-6 Monomer reactivity ratios of the binary copolymerizations of styrene (St)-methyl acrylate (MA)-methyl methacrylate (MMA) in toluene at various pressures and 335 K resulting from the improved curve-fitting I[27] and the linear regression method[28].

Pressure (MPa)	Improved curve-fitting I			Linear regression		
	r_1	r_2	$r_1 \cdot r_2$	r_1	r_2	$r_1 \cdot r_2$
			St-MA			
3.4	1.19 ± 0.03	0.09 ± 0.01	0.11 ± 0.04	1.20 ± 0.04	0.09 ± 0.01	0.11 ± 0.04
59	1.16 ± 0.02	0.11 ± 0.01	0.13 ± 0.03	1.12 ± 0.03	0.11 ± 0.00^3	0.12 ± 0.03
118	1.11 ± 0.02	0.13 ± 0.01	0.14 ± 0.03	1.10 ± 0.02	0.13 ± 0.00^3	0.14 ± 0.03
			St-MMA			
3.4	0.84 ± 0.02	0.36 ± 0.02	0.30 ± 0.04	0.86 ± 0.03	0.38 ± 0.02	0.33 ± 0.05
59	0.82 ± 0.02	0.39 ± 0.01	0.32 ± 0.03	0.82 ± 0.02	0.39 ± 0.01	0.32 ± 0.03
118	0.76 ± 0.01	0.41 ± 0.01	0.31 ± 0.02	0.77 ± 0.02	0.41 ± 0.01	0.32 ± 0.03
			MMA-MA			
3.4	2.48 ± 0.03	0.32 ± 0.00^4	0.79 ± 0.03	2.42 ± 0.03	0.31 ± 0.01	0.75 ± 0.04
59	2.41 ± 0.03	0.31 ± 0.00^5	0.75 ± 0.04	2.36 ± 0.03	0.31 ± 0.00^5	0.73 ± 0.04
118	2.39 ± 0.03	0.30 ± 0.00^6	0.72 ± 0.04	2.40 ± 0.02	0.30 ± 0.00^6	0.72 ± 0.03

The r values of St-MVK at 3.4 MPa and 335 K in toluene are:

$r_1 = 0.54 \pm 0.02$ $\quad r_2 = 0.22 \pm 0.01$ (Improved curve-fitting I)

$r_1 = 0.53 \pm 0.03$ $\quad r_2 = 0.22 \pm 0.01$ (Linear regression)

By applying the F test[29], it was concluded that all copolymerizations could be described by the Alfrey-Mayo model.

In particular the present r values for St-MMA differ considerably from the literature values observed under comparable conditions ($0.45 < r_1 < 0.64$, $0.44 < r_2 < 0.57$[30]). However, the azeotropic composition, which can be calculated from the present r values ($r_1 = 0.84$, $r_2 = 0.36$; $q_{az} = (1-r_2)/(1-r_1) = 4$), perfectly corresponds with q_{az} directly observed from the primary experimental data in Table 7-4. This supports our confidence in both procedures used for the calculation of r values (see also chapters 2 and 3). As a consequence, it is concluded that the discrepancy with literature values is attributable to the application of unreliable experimental techniques and/or calculation procedures, or unreported differences in experimental conditions.

Table 7-7 shows the activation volume differences of the St-MA-MMA binary copolymerizations using the improved curve-fitting I r values.

Table 7-7 Activation volume differences of binary copolymerizations of styrene (St)-methyl acrylate (MA)-methyl methacrylate (MMA) in toluene (pressure range: 3.4-118 MPa).

Monomer combination	$\Delta V_{11}^{\#} - \Delta V_{12}^{\#} = A$	$\Delta V_{22}^{\#} - \Delta V_{21}^{\#} = B$
St-MA	2.0 ± 0.3[a]	-8 ± 2[a]
St-MMA	2.0 ± 0.5	-2.8 ± 0.5
MMA-MA	0.9 ± 0.2	1.8 ± 0.3

[a] Estimated standard deviation.

The number-average degree of polymerization ($\overline{P}_n$) of St-MMA copolymers as a function of the mole fraction St in the copolymer at various pressures is given in Figure 7-4.

7.5 Discussion

7.5.1 Relations between structure and reactivity in (meth)acrylates and vinyl ketones; comparison with vinyl esters

In the copolymerization of a series of monomers (M_2) with a reference monomer (M_1) the ratio $1/r_1$ is a direct measure of monomer reactivity (see also chapter 6). The $1/r_1$ values of the copolymerizations of MVK, MA, and MMA with St, together with the results of the copolymerization of the homologous series of vinyl esters with ethylene as reference monomer are given in Table 7-8.

Table 7-8 Reactivity of methyl vinyl ketone, methyl acrylate, and methyl methacrylate toward the styrene macroradical and the reactivity of a homologous series of vinyl esters toward the ethylene macroradical[31,a].

$CH_2=\overset{R_1}{\overset{\mid}{C}}-\overset{O}{\overset{\|}{C}}-R_2$				$CH_2=CH-O-\overset{O}{\overset{\|}{C}}-R$		
	R_1	R_2	$1/r_1$[b]		R	$1/r_1$[c]
MVK	H	CH_3	1.89	VAc	CH_3	1.35
MA	H	OCH_3	0.85	VP	$CH_2(CH_3)$	1.48
MMA	CH_3	OCH_3	1.19	ViB	$CH(CH_3)_2$	1.64
				VPV	$C(CH_3)_3$	1.55

[a] All copolymerizations at 3.4 MPa and 335 K.
[b] Solvent: toluene.
[c] Solvent: *tert*-butyl alcohol.

When the CH_3 group in MVK is replaced by the more electron-donating OCH_3 group a decrease in monomer reactivity is observed. The greater reactivity of MMA over MA may be explained by hyperconjugation of the methyl group with the double bond. The results fit in well with the generally observed behavior of monomers possessing a $C=C-C=O$ group[4-9,13]. In most cases the relative reactivities are correlated with the Taft polar substituent constants of the monomers, as can be seen from Table 7-1. The results may be explained by greater polarization of the carbonyl group with increasing electron-donating ability of the substituent attached to the alkyl C atom next to the group. As a result, the conjugation of the vinyl group with the carbonyl group is decreased, so reducing the reactivity. Thus, in contrast to the vinyl esters a decreasing reactivity occurs despite the increasing electron density on the vinyl group. As a consequence, it may be concluded that resonance factors are of major importance in the relative reactivities of (meth)acrylates and vinyl ketones. However, according to Otsu and Tanaka[9], the values of the resonance substituent constants (E_R) of alkyl vinyl ketones are very close to each other, making it impossible to differentiate between the resonance effects pertaining to the various substituents. The reason for this apparent contradiction is not clear.

On the other hand, if resonance effects were the determining factor in the copolymerization of St (1) and MMA (2), r_1 (k_{11}/k_{12}) would be

$$\frac{\text{St}\cdot + \text{St}\ (k_{11})}{\text{St}\cdot + \text{MMA}\ (k_{12})} \qquad \frac{\text{MMA}\cdot + \text{MMA}\ (k_{22})}{\text{MMA}\cdot + \text{St}\ (k_{21})}$$

greater than 1 and r_2 (k_{22}/k_{21}) would be less than 1. The propagation reactions involving St monomer (with rates k_{11} and k_{21}) would be faster than the corresponding reactions involving MMA monomer (with rates k_{12} and k_{22}), because the resulting macroradical is more stabilized by resonance (see also Figure 7-1). However, the observed r_1 value for St-MMA is less than 1 (Table 7-6), pointing to the role of polar factors in the propagation rates. The St-MVK copolymerization shows similar behavior, whereas for St-MA r_1 is slightly above 1. However, it still may be inferred that also in the latter system polarity affects reactivity. Therefore, it must be concluded that in conjugated monomers the activation energy and pertaining reaction rate constants are affected both by resonance and polar factors.

In the other type of system, viz., the unconjugated monomers, reactivity is mainly governed by polar factors. The reactivity of the homologous series of vinyl esters toward both the ethylene macroradical[31] and the vinyl acetate[32] macroradical appears to be a function of the electron density on the double bond. By means of the *Q-e* scheme[33] (mindful of the limits of validity, e.g., $r_1 \cdot r_2 < 1$, of this scheme) it was found that the amount of resonance stabilization remains the same and that the electron density on the double bond increases upon increasing electron-donating character of the substituents. Furthermore, the vinyl ester reactivity order is susceptible to the polar character of the reference macroradical, which may be concluded from the fact that the reaction constant ρ^* may be both positive and negative[31]. In case of conjugated monomers the reactivity order remains the same toward any macroradical; ρ^* is positive (Table 7-1) regardless of the nature of the macroradical. This supports the suggestion that in case of conjugated monomers mainly resonance factors are important in the interpretation of the relative reactivities.

From Table 7-8 it might be inferred that conjugated and unconjugated monomers have comparable reactivities. However, in section 7.1 it was discussed that conjugated monomers are much more reactive than unconjugated monomers toward any macroradical. This apparent contradiction originates from the fact that the information obtained by means of copolymerization is restricted to the relative reactivity of two monomers with respect to the same macroradical. In Table 7-8 the binary systems contain reacting species which are either all conjugated or all unconjugated, and this explains the apparent similarity in the reactivities when the systems are compared.

Various attempts have been made to describe the reactivity of *individual* monomers and corresponding radicals by characteristic constants enabling a reliable description of structure-reactivity relations, which furthermore, would permit a prediction of copolymerization behavior. In section 2.4 the *Q-e* scheme[33] was compared with the *Patterns* method[34]. The former scheme was chosen because it is the most widely used scheme, whereas the latter method inherently provides a better approach to reactivity. This is achieved by using only experimentally accessible parameters and the assignment of different polarity parameters to radicals and monomers. In section 2.4 the difference between the *Q-e* scheme and *Patterns* was decisively shown by a comparison of the value of the *H* function of Mayo (eq. 2.13) experimentally observed and the values calculated by means of both schemes. The observed values correlate well with those calculated by means of *Patterns*, whereas the *Q-e* scheme completely fails to cope with the situation.

Table 7-9 Monomer reactivity ratios of the binary copolymerizations of styrene (St)-methyl acrylate (MA)-methyl methacrylate (MMA) calculated by the *Q-e* scheme[33] and the *Patterns* method[34] together with the *r* values observed at 3.4 MPa and 335 K with toluene as solvent.

Binary combination		*Q-e*	*Patterns*	Experimental
St-MA	r_1	0.70	0.42	1.19
	r_2	0.18	0.10	0.09
St-MMA	r_1	0.49	0.86	0.84
	r_2	0.48	0.43	0.36
MMA-MA	r_1	1.91	1.32	2.48
	r_2	0.49	0.42	0.32

In Table 7-9 the monomer reactivity ratios of the binary copolymerizations of St-MA-MMA calculated by both methods are given together with the r values experimentally observed at 3.4 MPa, 335 K and toluene as solvent. The Q and e values given by Greenley[35] have been used. This author claims the calculation of more precise values of Q and e by the application of a roundabout least squares technique applied to practically all the r values relevant to a selection of vinyl monomers. However, from Table 7-9 no definite conclusions can be drawn about the validity of either scheme for the prediction of individual r values. The correspondence between the experimental value of the H function of Mayo and the value calculated by means of *Patterns* appears to be excellent.

Mayo H factor for St-MA-MMA binary copolymerizations.

	Q–e	*Patterns*	Experimental
H	1 (by definition)	0.7	0.7 ± 0.1

The better fit of H as compared to the individual r values by using *Patterns* may be due to the effect of solvent on the various propagation reactions in the system St-MA-MMA. In this manner the overall-result might be that H becomes independent of solvent. However, a detailed interpretation of the effect of solvent in copolymerization is hampered by the fact that solvent may affect the reactivity of both monomers and radicals, and the transition states of all the propagation reactions. Only in the investigation of the effect of solvent on the Eth-VAc copolymerization has a monomer been used which has a reactivity unaffected by the nature of the solvent[36]. The variation of the r values with solvent could then be correlated with VAc reactivity. However, in the present copolymerizations the solvent also affects the reactivity of the reference monomer St. In addition, the variation of radical reacticity and the stabilization of the transition state with solvent has to be considered. For example, a more polar solvent may increase the polarity of the carbonyl group, resulting in a decreased resonance of the carbonyl group with the reacting double bond. As a consequence, monomer reactivity is decreased. On the other hand, the transition state of the propagation reaction may be more stabilized with increased polarity of the solvent, leading to a higher gain in resonance stabilization on going from the initial state to the transition state, and therefore to a greater propagation rate. As a consequence, the overall-result may vary with the solvent. In fact, as many interpretations have been given as investigations have been carried out, as appears from a review by Madruga et al.[18].

From the foregoing it may be concluded that the investigations of the solvent-effect on reactivity in free-radical copolymerization requires the use of Eth as comonomer. However, the reactivities of Eth and (meth)acrylates and vinyl ketones are too disparate to allow a reliable determination of *r* values. Therefore, until this problem has been solved satisfactorily, the results of the investigations of the solvent-effect on the reactivity of (meth)acrylates and vinyl ketones should be interpreted with great care.

7.5.2 Effects of pressure on the system styrene-methyl acrylate-methyl methacrylate

As has been shown by the experiments discussed in section 7.5.1, the *relative* reactivities of conjugated monomers appear to be influenced by resonance effects induced by polar factors. Moreover, the height of the activation energy barriers in the various addition reactions, and with that the *absolute* magnitude of the *r* values, are a function of polar *and* resonance factors. On the other hand, the sign of the activation volume differences A and B for St-MA and St-MMA given in Table 7-7 show the more exothermic reactions, forming the more stable St macroradical, to be accompanied by a less negative activation volume (earlier transition state) as required by the Hammond postulate. This is in full agreement with the potential energy calculations summarized in Figure 7-1. Thus, on going from the transition state to the final state the gain in resonance stabilization becomes the more important factor.

To summarize, in the copolymerization of St with (meth)acrylates and vinyl ketones the <u>height</u> of the activation energy barrier, and with that the *r* values are governed by *resonance and polar* factors. Furthermore, the <u>location</u> of the transition state on the reaction coordinate, and with that the activation volume is mainly governed by *resonance* factors (Figure 7-3.A). In other words, in conjugated monomers a more exothermic reaction has a more positive activation volume, but there is not a clear correlation with the activation energy.

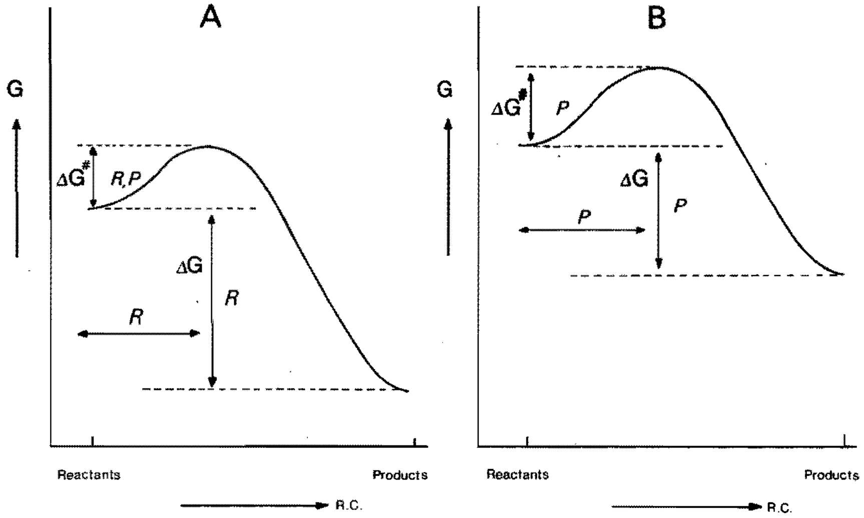

Figure 7-3 Factors affecting the various processes on going from the initial state to the final state for copolymerizations involving conjugated (Figure 7-3.A) and unconjugated monomers (Figure 7-3.B); *R*: (mainly) resonance factors, *P*: (mainly) polar factors.

A different situation occurs when considering unconjugated monomers, viz., vinyl esters, where the absolute magnitude of the r values as well as the magnitude of the activation volume are a function of polar factors (chapter 6). Thus, it can be inferred that the behavior of these unconjugated monomers is a straightforward demonstration of the Hammond postulate since in this case the process of going from the initial state to the transition state (in terms of $\Delta G^{\#}$ and $\Delta V^{\#}$) as well as the process of going from the initial to the final state (in terms of ΔG) are affected by polar factors in the same manner (Figure 7-3.B). In this way activation energy, activation volume and exothermicity are directly related. This is comparable with the results of Le Noble and Asano's example of the Menshutkin reaction[37] (see also chapter 4), where the correlation of $\Delta G^{\#}$, ΔG, and $\Delta V^{\#}$, in terms of the Hammond postulate, develops because the steric effect is dominant.

An equally straightforward interpretation is not possible for the systems St-MA and St-MMA in which the activation volume correlates as expected with the exothermicity, but not with the activation energy. This is a partial deviation from the Hammond postulate, in the form in which it was expressed by Asano and Le Noble[37]; but the evidence discussed above, concerning the role of resonance and polar factors, is considered to support the possibility that the postulate can be refined and extended to include the more complex behavior of systems in which reactivity is not dominated by a single factor (e.g. polarity, resonance stabilization or steric hindrance). This requires adoption of the principle that the Hammond postulate remains valid in comparisons of those features of the reaction processes which are governed by similar reactivity factors. In these conjugated systems it appears that the activation volume and the reaction ΔG are dominated by resonance factors, while the height of the activation energy barrier is determined by both polar and resonance factors. The modified Hammond postulate can thus account for the experimental result that $\Delta V^{\#}$ and the exothermicity show a correlation, while $\Delta V^{\#}$ and the reaction rates (r values) do not. Confirmation of the extended postulate will require further experimental evidence.

It may indeed be expected that in case of the copolymerization of monomers exhibiting relatively small differences in resonance factors, as e.g., MMA-MA, the polar effects will show up more strongly, and a possible dominance of either effect may not be distinguishable as clearly as in the systems St-MA and St-MMA. This is confirmed by the results of the MMA-MA copolymerization (Table 7-7), where a more stable radical only gives rise to an earlier transition state with MMA macroradical ($\Delta V_{11}{}^{\#} - \Delta V_{12}{}^{\#} = +0.9 \pm 0.2$ cm^3/mole), but where the contrary is observed with respect to the MA macroradical ($\Delta V_{22}{}^{\#} - \Delta V_{21}{}^{\#} = +1.8 \pm 0.3$ cm^3/mole).

In conclusion, we may summarize the present results as follows. In the vinyl ester copolymerization we have shown that polar factors predominate in $\Delta G^{\#}$, ΔG and $\Delta V^{\#}$, whereas in an example of the Menshutkin reaction[37] the steric effect is dominant. Both investigations have in common that one single factor governs all features of the reaction process. This allows of a straightforward interpretation of the results in terms of the Hammond postulate and is in full agreement with Evans's potential energy calculations (Figure 7-1)[2,3]. In our study on conjugated monomers, however, an interplay of resonance and polar factors in $\Delta G^{\#}$, ΔG, and $\Delta V^{\#}$, is found. This indicates an interesting line of development, that needs considerably broader experimental basis as well as an extended theoretical treatment, e.g., the modification of Evans's calculations to incorporate polar, steric, and resonance effects.

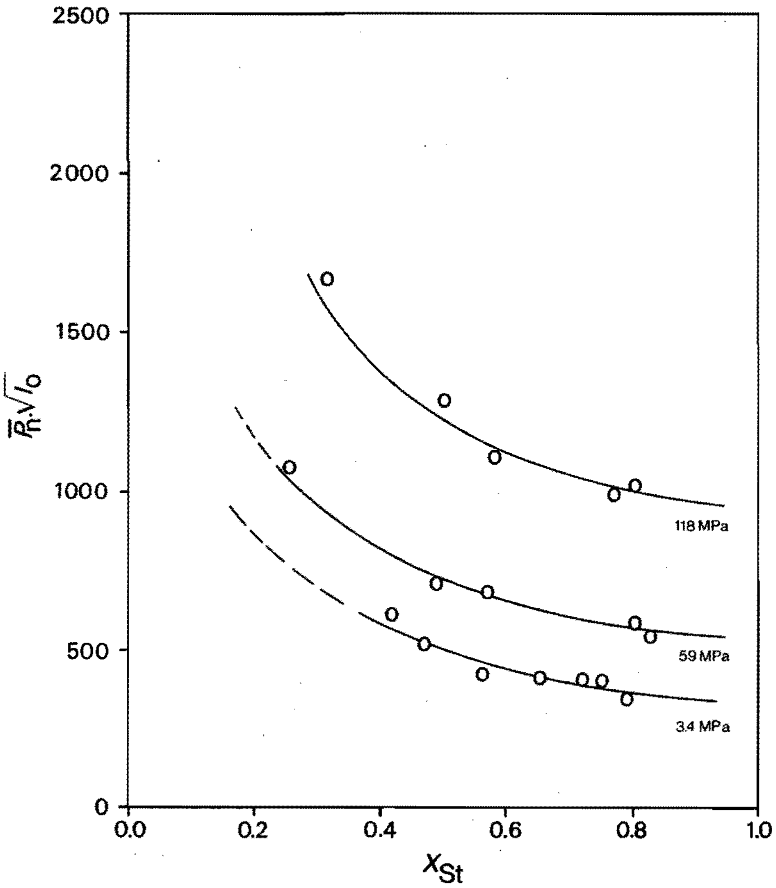

Figure 7-4 "Reduced" number-average degree of polymerization ($\overline{P}_n \cdot \sqrt{I_o}$) of styrene-methyl methacrylate copolymers vs. the mole fraction styrene (x_{St}) in the copolymer at various pressures. (I_o in mmole/dm^3).

7.5.3 Effect of pressure on the number-average degree of polymerization

In Figure 7-4 the relation is shown between the "reduced" number-average degree of polymerization $\overline{P}_n \cdot \sqrt{I_o}$ and the mole fraction St (x_{St}) in St-MMA copolymers at the three pressure levels. $\overline{P}_n$ was calculated from the number-average molecular weight ($\overline{M}_n$) and the overall-composition of the copolymer. For the purpose of comparison between the various results, it is preferable to consider $\overline{P}_n \cdot \sqrt{I_o}$ instead of $\overline{P}_n$, because in polymerization the kinetic chain length is inversely proportional to $\sqrt{I}$. I_o is the initial initiator concentration in mmole/dm^3. It appears that at each pressure level $\overline{P}_n \cdot \sqrt{I_o}$ decreases by a factor of about 2.5 on going from x_{St} is 0 to 1. Eq. 7.3 shows that $\overline{P}_n$ is a complex function of many variables[38]:

$$1/\overline{P}_n = C_q + S_q \cdot [S]/[M_2] + T_q \cdot R_p/[M_2]^2 \tag{7.3}$$

In this equation T_q contains the r values and various ratios of termination rate constants. Moreover, T_q and the chain transfer constants C_q and S_q depend on the monomer feed ratio q and thus on x_{St}. It is not clear, which factors and to what extent will affect $\overline{P}_n$ resulting in the observed variation of $\overline{P}_n$ with x_{St}.

Table 7-10 "Reduced" number-average degree of polymerization ($\overline{P}_n \cdot \sqrt{I_o}$) of styrene-methyl methacrylate at mole fraction styrene (x_{St}) of 0.5, and various pressures.

Pressure (MPa)	$\overline{P}_n \cdot \sqrt{I_o}$ [a]
3.4	480 (1.00)
59	740 (1.54)
118	1220 (2.54)

[a] In parenthesis the values for $\overline{P}_n \cdot \sqrt{I_o}$ relative to the value at 3.4 MPa are given.

The variation of $\overline{P}_n \cdot \sqrt{I_o}$ with pressure allows of the calculation of the overall-activation volume $\Delta V^{\#}$ at each mole fraction x_{St}. In Table 7-10 the values of $\overline{P}_n \cdot \sqrt{I_o}$ and the relative values of $\overline{P}_n \cdot \sqrt{I_o}$ with respect to $\overline{P}_n \cdot \sqrt{I_o}$ at 3.4 MPa are given for $x_{St} = 0.5$. The activation volumes calculated from various pressure intervals are summarized in Table 7-11, and visualized in Figure 7-5.

Table 7-11 Overall activation volumes calculated from various pressure intervals at mole fraction styrene in the copolymer of 0.5.

Pressure range (MPa)	$\Delta V^{\#}$ (cm^3/mole)
3.4 - 59	-21.8
3.4 - 118	-22.6
3.4 - 118[a]	-22 ± 1[b]

[a] All data points are considered, assuming a linear course of ln ($\overline{P}_n \cdot \sqrt{I_o}$) vs. pressure.
[b] Estimated standard deviation.

The activation volumes at x_{St} = 0.3, 0.5, and 0.8 and the literature value for the bulk homopolymerization of St[17,35] are given below.

Overall activation volumes $\Delta V^{\#}$ pertaining to $\overline{P}_n$, determined from St-MMA copolymers of different compositions.

x_{St}	0.3	0.5	0.8	1[17,35]
$\Delta V^{\#}$ (cm^3/mole)	-19 ± 3	-22 ± 1	-24 ± 2	-20

Mindful of the accuracy of the activation volumes it may be stated that there is a tendency for $\Delta V^{\#}$ to become more negative as x_{St} goes from 0 to 1. The results are in good agreement with the value of -20 cm^3/mole given for St[20,39].

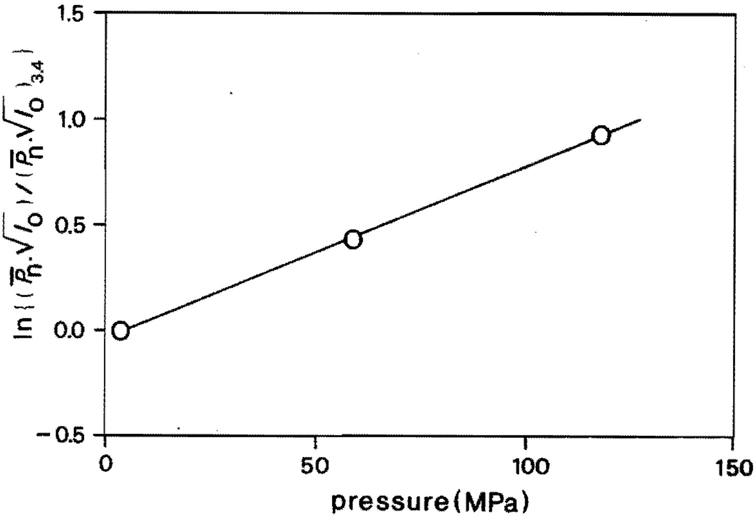

Figure 7-5 Relative "reduced" number-average degree of polymerization of styrene-methyl methacrylate copolymers vs. pressure at mole fraction styrene in the copolymer of 0.5.

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Appendix

A The differential copolymer equation

Independently, Alfrey and Goldfinger[1], and Mayo and Lewis[2], derived the differential copolymer equation under the following conditions:

- only propagation steps are considered, while consumption of monomers by initiation, reinitiation and termination is negligible; this means a sufficiently high molecular weight;
- the reactivity of a copolymer chain end radical is independent of the chain length (Flory principle), and determined only by the ultimate unit of the macroradical;
- both monomers react with radicals according to the same, bimolecular mechanism, and the propagation reactions are irreversible;
- the steady-state principle is assumed to be valid; this means that the rate of change of the radical concentration of $\sim M_1\cdot$ and $\sim M_2\cdot$ is small as compared to the rates of radical production and consumption.

Under these conditions only four different chain propagation reactions have to be considered:

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1\cdot$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_1\cdot$$

By definition, the reaction rate is[3,4]:

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

where r is the reaction rate in mole.dm^{-3}.s^{-1}; V is the reaction volume in dm^3; n is the number of moles and t is the time in seconds.

For a second order bimolecular reaction:

$$r = -\frac{1}{V}\cdot\frac{dn_a}{dt} = kc_a c_b$$

and

$$\frac{-dn_a}{dt} = kVc_a c_b = kn_a c_b$$

where k is the reaction rate constant in mole.dm^{-3}.s^{-1} and c denotes concentration in mole.dm^{-3}.

The rates of consumption of both monomers are then given by:

$$\frac{-dn_1}{dt} = k_{11}n_1[M_1\cdot] + k_{21}n_1[M_2\cdot] \tag{A.1}$$

$$\frac{-dn_2}{dt} = k_{12}n_2[M_1\cdot] + k_{22}n_2[M_2\cdot] \tag{A.2}$$

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

$$k_{12}[\sim M_1\cdot]n_2 = k_{21}[\sim M_2\cdot]n_1$$

or

$$[\sim M_1\cdot] = \frac{k_{21}}{k_{12}}\cdot\frac{n_1}{n_2}\;[\sim M_2\cdot] \tag{A.3}$$

The composition of the instantaneously formed copolymer is:

$$\frac{-\frac{dn_1}{dt}}{-\frac{dn_2}{dt}} = \frac{dn_1}{dn_2} \tag{A.4}$$

By combining eqs. A.1, A.2, A.3, and A.4 the radical concentrations can be eliminated, yielding:

$$\frac{dn_1}{dn_2} = \frac{r_1(n_1/n_2) + 1}{r_2(n_2/n_1) + 1} \tag{A.5}$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$.

B The integrated copolymer equation

The differential copolymer equation (eq. A.5) can be integrated yielding an exact relationship between the monomer feed composition (q) and the degree of conversion (f). The integral can be obtained in the following way:

$$\frac{dq}{df_2} = \frac{d(n_1/n_2)}{df_2} = \frac{n_{20}}{100}\left(\frac{n_2 dn_1 - n_1 dn_2}{n_2^{\,2}}\right)\Big/ - dn_2$$

$$= \frac{-n_{20}}{100 \cdot n_2}\left(\frac{dn_1}{dn_2} - \frac{n_1}{n_2}\right)$$

$$= \frac{1}{100 - f_2}\left(q - \frac{dn_1}{dn_2}\right)$$

with the conversion based on monomer 2 defined as $f_2 = 100 \cdot (1 - n_2/n_{20})\%$. The subscript zero indicates initial conditions. This can be arranged to:

$$\frac{df_2}{100 - f_2} = \frac{dq}{\left(q - \frac{dn_1}{dn_2}\right)}$$

With equation A.5 for dn_1/dn_2 this integral can be evaluated analytically[4,5], yielding:

$$f_2 = 100 \cdot \left[1 - \left(\frac{q}{q_o}\right)^{-x_2-1} \left(\frac{x_2 q - x_1}{x_2 q_o - x_1}\right)^{x_1+x_2+1}\right]$$

where f_{20} is set equal to zero; $x_1 = 1/(r_1-1)$ and $x_2 = 1/(r_2-1)$ under the constraints $r_1 \neq 1$ and $r_2 \neq 1$.

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Summary

Copolymerization and high-pressure study are shown to be important tools in revealing relations between structure and reactivity of vinyl monomers and corresponding radicals. A detailed investigation of reactivity requires a reliable determination of the monomer reactivity ratios (*r* values) describing the copolymerization behavior of vinyl monomers. This is achieved by applying nonlinear least squares to the integrated copolymer equation. Furthermore, it is necessary to take into account experimental errors in all measured variables. These conditions are fulfilled in three, recently published, calculation procedures of which the most efficient one, viz., the improved curve-fitting I procedure is used in the present investigation.

The information obtained by means of copolymerization is restricted to pairs of monomers. Several approaches have been developed to describe the reactivity of the individual monomers and radicals. The most widely used scheme, viz., the *Q-e* scheme is compared with *Patterns*. The latter method inherently provides a better approach to reactivity, by using only experimentally accessible parameters and the assignment of different polarity parameters to radicals and monomers.

Application of the improved curve-fitting I procedure for the calculation of *r* values requires the use of a high-speed computer. Therefore, research for pencil and paper procedures has continued. As a result, a new, simple and yet reliable method for the calculation of *r* values, based on the observation of the linearity of the plot $\ln n_1$ vs. $\ln n_2$ is developed. For all copolymerizations investigated, the results of the new linear regression method are in good agreement with those obtained by means of the improved curve-fitting I method. The range of validity of the linear regression method is determined by comparison with the improved curve-fitting I procedure by means of simulated copolymerization experiments. The method, given the experimental setup and error structure described, appears to be applicable when the product of the *r* values is between 0.001 and 2, provided both monomer conversions are large enough compared with the measurement error.

The effect of pressure on the rate constant of a chemical reaction is governed by the sign and magnitude of the activation volume, $\Delta V^{\#}$. In polymerization reactions this is illustrated by a discussion of the effect of pressure on the basic steps, i.e., initiation, propagation, and termination. Furthermore, the effect of solvent and steric hindrance on the activation volume is discussed. In copolymerization the pressure-effect on the reactivity of monomers and radicals is governed by differences in activation volumes. Major attention is paid to the prediction of the effect of pressure on *r* values. Two existing hypotheses are compared with a new approach based on the Hammond postulate. Herein differences in monomer reactivity are directly related to differences in activation volumes whereas the magnitude of the observed effects is dependent on the reactivity of the radicals.

In order to improve the determination of high-pressure *r* values a sequential sampling of reaction mixtures under high pressure, followed by on-line GLC analysis of the sample is developed. The merits and drawbacks of the new method are compared with those of the "quenching" method previously used. In conclusion, the "sequential sampling" method is preferred over the "quenching" method.

The experimental techniques and computational procedures for a reliable determination of *r* values under a wide range of experimental conditions are now available. This allows of a detailed investigation of monomer reactivity in free-radical copolymerization. As vinyl monomers can be roughly divided into two classes of monomers, viz., conjugated and unconjugated monomers, both types have been investigated in the present study.

The copolymerization of a homologous series of vinyl esters (unconjugated monomers) has been thoroughly investigated in our laboratory. It appears that mainly polar factors are important in the interpretation of the relative reactivities of the monomers. The exceptional position of vinyl pivalate was previously explained by sterically hindered addition reactions. However, additional research points to an explanation based on the role of the solvent *tert*-butyl alcohol (both monomer and solvent possess a *tert*-butyl group). The effect of pressure on ethylene-vinyl ester copolymerizations in *tert*-butyl alcohol is explained by means of the Hammond postulate. In this way there is a full correlation of activation energy ($\Delta G^{\#}$), activation volume ($\Delta V^{\#}$) and exothermicity (ΔG) in the relevant propagation reactions.

An equally straightforward interpretation of the pressure-effect is not possible for conjugated monomers. In the system styrene-methyl acrylate and styrene-methyl methacrylate $\Delta V^{\#}$ correlates with ΔG, but not with $\Delta G^{\#}$, because reactivity is not dominated by a single factor (e.g. polarity, resonance stabilization or steric hindrance). It appears that $\Delta V^{\#}$ and ΔG are dominated by resonance factors, while the height of the activation energy barrier is determined by both polar and resonance factors.

From the results of the investigation of conjugated and unconjugated monomers it may be concluded that the Hammond postulate remains valid when comparing those features of the reaction processes which are governed by similar reactivity factors.

Samenvatting

Copolymerisatie en de bepaling van de invloed van druk op de daarbij behorende kinetische parameters blijken bij uitstek geschikt voor de bestudering van verbanden tussen structuur en reactiviteit van vinylverbindingen en daaruit gevormde radicalen. Een diepgaand onderzoek van reactiviteit maakt een betrouwbare bepaling noodzakelijk van de monomere reactiviteitsverhoudingen (r waarden), die het copolymerisatiegedrag van twee monomeren beschrijven. Dit kan bereikt worden, door gebruik te maken van een berekeningsmethode die gebaseerd is op de geïntegreerde copolymerisatievergelijking en die rekening houdt met meetfouten in alle variabelen. Aan deze voorwaarden wordt voldaan in drie, recent gepubliceerde, berekeningsmethoden, waarvan de meest efficiënte, de improved curve-fitting I methode, in het huidige onderzoek gebruikt is.

Bij copolymerisatie wordt informatie verkregen over de relatieve reactiviteit van twee monomeren. Diverse hypothesen zijn ontwikkeld om de reactiviteit van de afzonderlijke monomeren en radicalen te beschrijven. Het meest gebruikte schema (Q-e schema) wordt vergeleken met *Patterns*. De laatstgenoemde methode voorziet in een inherent betere beschrijving van reactiviteit door alleen experimenteel toegankelijke parameters te gebruiken en de toekenning van verschillende polariteitsparameters aan radicalen en monomeren.

Toepassing van de improved curve-fitting I methode maakt gebruik van een computer noodzakelijk. Onderzoek naar eenvoudige methoden, waarvoor geen computer nodig is, werd daarom voortgezet. Dit heeft geleid tot een nieuwe, eenvoudige en toch betrouwbare methode voor de berekening van r waarden, die gebaseerd is op het waargenomen lineaire verband tussen ln n_1 en ln n_2. Voor alle onderzochte polymerisaties blijken de resultaten van de nieuwe lineaire regressie methode en die verkregen met behulp van de improved curve-fitting I methode in goede overeenstemming met elkaar te zijn. De grenzen van toepasbaarheid van de nieuwe methode zijn bepaald door vergelijking met de improved curve-fitting I methode door middel van nagebootste copolymerisatie-experimenten. Gebaseerd op de beschreven experimentkeuze en fouten-structuur, blijkt de methode toepasbaar te zijn als het product van de *r* waarden ligt tussen 0,001 en 2, mits de omzetting van beide monomeren groter is dan de meetfout.

De invloed van druk op de snelheidsconstante van een chemische reactie wordt bepaald door het teken en de grootte van het activeringsvolume $\Delta V^{\#}$. Voor polymerisatiereacties wordt dit geïllustreerd aan de hand van een beschouwing van de drukinvloed op de elementaire reactiestappen: initiatie, propagatie en terminatie. Bovendien wordt de invloed van oplosmiddel en sterische hindering op $\Delta V^{\#}$ besproken. In copolymerisatie wordt de drukinvloed op de reactiviteit van monomeren en radicalen bepaald door verschillen in activeringsvolumina. Veel aandacht is besteed aan de voorspelling van de drukinvloed op *r* waarden. Twee bestaande hypothesen zijn vergeleken met een nieuw concept gebaseerd op het Hammond postulaat. In deze laatste methode zijn verschillen in monomeerreactiviteit direct gerelateerd aan verschillen in $\Delta V^{\#}$'s, terwijl de grootte van de waargenomen effecten afhankelijk is van de reactiviteit van de radicalen.

Teneinde de bepaling van hoge-druk *r* waarden te verbeteren, is een methode ontwikkeld voor de sequentiële bemonstering van reactiemengsels onder hoge druk, gevolgd door "on-line" GLC analyse van het monster. De voor- en nadelen van de nieuwe methode worden vergeleken met die van de voordien gebruikte "quenching" methode. Er wordt geconcludeerd dat de "sequential sampling" methode de voorkeur verdient boven de "quenching" methode.

De experimentele technieken en berekeningsmethoden voor een betrouwbare bepaling van *r* waarden, over een breed gebied van reactieomstandigheden, staan nu ter beschikking. Dit maakt een gedetailleerde bestudering van monomeerreactiviteit in vrije-radicaal copolymerisatie mogelijk. Omdat vinylmonomeren globaal verdeeld kunnen worden in twee klassen monomeren, geconjugeerde en ongeconjugeerde monomeren, zijn beide typen onderzocht in het huidige onderzoek.

De copolymerisatie van een homologe serie vinylesters (ongeconjugeerde monomeren) werd diepgaand onderzocht in ons laboratorium. Het blijkt dat voornamelijk polaire factoren van belang zijn voor de interpretatie van de relatieve reactiviteiten van de monomeren. De uitzonderingspositie van vinylpivalaat werd voorheen verklaard met sterisch gehinderde additiereacties. Aanvullend onderzoek leidt tot een verklaring gebaseerd op de rol van het oplosmiddel *tert*-butylalcohol (zowel monomeer als oplosmiddel bezitten een *tert*-butylgroep). De drukinvloed op etheen-vinylester copolymerisaties in *tert*-butylalcohol kan worden verklaard met behulp van het Hammond postulaat. Hieruit volgt een volledige correlatie van activeringsenergie ($\Delta G^{\#}$), activeringsvolume ($\Delta V^{\#}$) en exothermiciteit (ΔG) in de onderhavige propagatiereacties.

Een gelijksoortige, rechtstreekse interpretatie van de drukinvloed is niet mogelijk voor geconjugeerde monomeren. In het systeem styreen-methylacrylaat-methylmethacrylaat blijkt $\Delta V^{\#}$ gecorreleerd met ΔG, maar niet met $\Delta G^{\#}$, omdat de reactiviteit van monomeren en radicalen niet beheerst wordt door één enkele factor (bijv. polariteit, resonantiestabilisatie of sterische hindering). Het blijkt dat $\Delta V^{\#}$ en ΔG bepaald worden door resonantiefactoren, terwijl de grootte van de activeringsenergie afhankelijk is van zowel polaire als resonantiefactoren.

Uit de resultaten van het onderzoek van geconjugeerde en ongeconjugeerde monomeren kan geconcludeerd worden dat het Hammond postulaat zijn geldigheid behoudt wanneer die aspecten van de reactieprocessen met elkaar vergeleken worden, welke bepaald worden door dezelfde reactiviteitsfactoren.

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Levensbericht

De schrijver van dit proefschrift werd op 28 januari 1954 in Kampen geboren. Hij bezocht aldaar het Johannes Calvijn Lyceum, waar hij in 1971 het diploma HBS-B behaalde. In hetzelfde jaar begon hij met de studie Scheikunde aan de Rijksuniversiteit te Utrecht.

Het kandidaatsexamen (S1) werd afgelegd op 16 december 1974. Het doctoraalexamen werd behaald op 13 december 1976, met als hoofdvak organische chemie (Prof.dr. G.J.M. van der Kerk) en als bijvak theoretische chemie (Prof.dr. D.H.W. den Boer).

Vanaf 1 januari 1977 is hij als wetenschappelijk ambtenaar in dienst van SON/ZWO werkzaam geweest in de groep Kunststoftechnologie van de vakgroep Chemische Technologie aan de Technische Hogeschool Eindhoven, alwaar het in dit proefschrift beschreven onderzoek werd verricht.

STELLINGEN

1. Een onderzoek met als doel orde te scheppen in het grote aantal berekeningsmethoden voor r waarden is zeer wenselijk[*]. De aanpak van McFarlane et al.[**], waarbij geen rekening gehouden wordt met een verloop in de monomere voedingssamenstelling, is echter zinloos.

   [*] Dit proefschrift, hoofdstuk 2

   [**] R.C. McFarlane, P.M. Reilly en K.F. O'Driscoll, *J. Polym. Sci. Polym. Chem. Ed.*, 18, 251 (1980)

2. De conclusie van Rounsefell and Pittman[*], dat de copolymerisatie van 2,3,4-trimethyl-3-pentylmethacrylaat met styreen beschreven kan worden met een "penultimate"-model, wordt niet ondersteund door de gepubliceerde waarnemingen[*].

   [*] Th.D. Rounsefell en Ch.U. Pittman, Jr., *J. Macromol. Sci. Chem.*, A13, 153 (1979)

3. De waarde van onderzoek naar de inbouw van aan het synthesegas toegevoegde olefinen in koolwaterstoffen, met als doel de voor de Fischer-Tropsch synthese belangrijke reactie-intermediairen te identificeren[*,**], moet gering worden geacht.

   [*] J.G. Ekerdt en A.T. Bell, *J. Catal.*, 62, 19 (1980)

   [**] W. Keith Hall, R.J. Kokes en P.H. Emmett, *J. Am. Chem. Soc.*, 82, 1027 (1960)

4. Het veronderstelde, gunstige effect van de toepassing van mangaanftalocyanine op de ontleding van waterstofperoxide tijdens de katalytische autoxidatie van thiolen*, moet ernstig worden betwijfeld.

* Nederlandse octrooiaanvrage, 7608824 (1976); *Chem. Abstr.*, 89, 117037W (1978)

5. Het is onwaarschijnlijk, dat de door Gaspard et al.* gebruikte synthesemethode het door de auteurs veronderstelde kopertetracarboxyftalocyanine heeft opgeleverd**.

* S. Gaspard, M. Verdaguer en R. Viovy, *J. Chim. Phys.*, 11-12, 1740 (1972)

** J.H. Schutten en J. Zwart, *J. Mol. Catal.*, 5, 109 (1979)

6. Patino-Leal et al.* beweren ten onrechte, dat de methode van Van der Meer et al.** voor de berekening van parameters in modellen met fouten in alle veranderlijken, de opslag van grote matrices en het gebruik van complexe optimaliseringsmethoden*** vereist.

* H. Patino-Leal, P.M. Reilly en K.F. O'Driscoll, *J. Polym. Sci. Polym. Lett. Ed.*, 18, 219 (1980)

** R. van der Meer, H.N. Linssen en A.L. German, *J. Polym. Sci. Polym. Chem. Ed.*, 16, 2915 (1978); H.N. Linssen, Proefschrift, Technische Hogeschool Eindhoven, 1980

*** H.I. Britt en R.H. Luecke, *Technometrics*, 15, 233 (1973)

7. De unieke omstandigheid, dat uit atactisch, d.w.z. via radicaal-(co)polymerisatie verkregen, polyvinylalcohol en vinylalcoholetheen copolymeren semi-kristallijne polymere materialen kunnen worden verkregen, wordt, hoewel reeds lang bekend*, nog onvoldoende benut.

* C.W. Bunn en H.S. Peiser, *Nature*, 159, 161 (1947)

8. De conclusie van Wales, dat de groeisnelheid van oppervlaktecrazes alleen bepaald wordt door de aangelegde spanning*, gaat ten onrechte voorbij aan de onderlinge beïnvloeding van de crazes.

   * J.L.S. Wales, *Polymer*, 21, 684 (1980)

9. Aan de samenwerking tussen kerken liggen in een aantal gevallen financiële motieven ten grondslag. De veronderstelling hierbij, dat *economische* verbondenheid ook de *oecumenische* gedachte zal dienen, lijkt meer gebaseerd op de taalkundige verwantschap van beide kenmerken, dan op de huidige praktijk.

10. De meeste onderzoeken naar de relatie tussen voeding en gezondheid zijn gebaseerd op de vooronderstelling dat er lineaire verbanden bestaan tussen twee veranderlijken*. Daar aangenomen mag worden dat elke stof zijn eigen optimum kent (zoals aangetoond voor vitamine A en selenium*) en er relaties tussen meerdere veranderlijken bestaan (het effect van selenium wordt tegengewerkt door zink*), moet worden getwijfeld aan de waarde van voedingsadviezen die op grond van dergelijke onderzoeken gegeven worden.

   * O.G. Meyerer en G. Broekhuizen, "De relatie tussen voeding en gezondheid", *Intermediair*, 25 juli, 1 (1980)

11. Wanneer er in Nederland roofdieren leefden die per jaar ca. 1800* mensen zouden verscheuren, dan mag verondersteld worden dat die zo spoedig mogelijk in dierentuinen en wildparken ondergebracht zouden worden. Evenzo zou voor auto's en automobilisten moeten gelden dat alleen de meer tamme combinaties op de openbare weg toegelaten worden.

   * aantal verkeersslachtoffers onder automobilisten, fietsers en voetgangers in 1978; bron: Statistisch zakboek 1979

Eindhoven, 9 januari 1981 J. Schrijver