Copolymerization of Ethylene and Vinyl Acetate at Low Pressure: Determination of the Kinetics by Sequential Sampling

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Synopsis

In behalf of a detailed study on the course of copolymerization reactions, this paper describes an improved and generally applicable experimental method and an efficient computational procedure to match. The experimental method is based on quantitative gas chromatography, and permits frequent measurement of the monomer feed composition throughout (co)polymerization processes at pressures up to 40 kgf/cm² (= 38.7 atm). The given method is applied to the study of the radical copolymerization of ethylene with vinyl acetate in a series of kinetic experiments, at 62°C and 35 kgf/cm² (= 33.9 atm) in tert-butyl alcohol, in which 20-40% conversion is reached. Monomer feed composition and degree of conversion are entered into a computational procedure based on nonlinear least-squares methods applied to the integrated version of the copolymer equation. The experimental data, covering a region of ethylene molar feed fractions between 0.24 and 0.74 and copolymer concentrations up to 8 wt-%, are precisely consistent with the usual model. The respective reactivity ratios are $r_\text{e} = 0.743 \pm 0.005$ and $r_\text{v} = 1.515 \pm 0.007$.

INTRODUCTION

Although the free-radical copolymerization of ethylene and vinyl acetate has been known since 1938,¹ the copolymerization behavior has never been investigated thoroughly. The values of the monomer reactivity ratios presented in Table I are contradictory and unsurveyable and possibly depend on the often unknown reaction conditions under high pressure.

In addition, the copolymerization of ethylene with vinyl acetate has been generally presumed to obey the Mayo-Alfrey model,⁶,⁷ and the consistency of the experimental data with this model was not proved.

Moreover, the intersection method⁶,⁸ and the other procedures⁹ generally used to study copolymerization reactions are approximative⁹,¹⁰ and deficient in determining $r$ values with sufficient accuracy. The common experimental techniques also fail when gaseous monomers are involved.

The new experimental technique and the matching computational procedure described in this paper allow a detailed study on the course of co-
TABLE I

<table>
<thead>
<tr>
<th>Sources</th>
<th>$r_e$</th>
<th>$r_v$</th>
<th>$r_{e}r_{v}$</th>
<th>Temp, Pressure, °C</th>
<th>kgf/cm²</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burkhart and Zutty²</td>
<td>1.07</td>
<td>1.08</td>
<td>1.16</td>
<td>90</td>
<td>1000</td>
<td>Toluene</td>
</tr>
<tr>
<td>Terteryan et al.³</td>
<td>0.77</td>
<td>1.02</td>
<td>0.79</td>
<td>70</td>
<td>400</td>
<td>Benzene</td>
</tr>
<tr>
<td>Terteryan et al.³</td>
<td>0.97</td>
<td>1.02</td>
<td>0.99</td>
<td>130</td>
<td>400</td>
<td>Benzene</td>
</tr>
<tr>
<td>Brown and Ham⁴</td>
<td>1.01</td>
<td>1.02</td>
<td>1</td>
<td>150</td>
<td>840</td>
<td>—</td>
</tr>
<tr>
<td>Erussalimsky et al.⁵</td>
<td>0.16</td>
<td>1.14</td>
<td>0.18</td>
<td>60</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>Erussalimsky et al.⁵</td>
<td>0.70</td>
<td>3.70</td>
<td>2.59</td>
<td>60</td>
<td>1200</td>
<td>—</td>
</tr>
<tr>
<td>This investigation</td>
<td>0.74</td>
<td>1.51</td>
<td>1.12</td>
<td>62</td>
<td>35</td>
<td>TBA</td>
</tr>
</tbody>
</table>

Polymerization reactions up to 20–40% conversion and yield high accuracy in determining $r$ values and thus in model testing. The advantages of the present method include the omission of copolymer analysis with its accompanying errors. When gaseous monomers are involved the method is particularly favorable.

The present investigation provides a basis for future research on the influence of pressure on the kinetics of (co)polymerization.

**EXPERIMENTAL**

**Principles of Operation**

A schematic diagram of the equipment is shown in Figure 1. The reactor is a vertically placed cylindrical stainless steel vessel provided with a piston. The upper compartment (approximately 750 cm³) serves as reaction chamber, the lower to control the pressure. The liquid monomer (vinyl acetate) and the solvent (tert-butyl alcohol, TBA), containing the radical initiator ($\alpha,\alpha'$-azobisisobutyronitrile), were introduced into the reaction chamber. The approximate amount of gaseous monomer (ethylene) required was dissolved in the liquid at 30 kgf/cm² (≈29.0 atm) and 62°C. The requirement of a closed reaction system was met by venting the gas phase completely at constant pressure. Next, the liquid phase was pressurized up to the reaction pressure of 35 kgf/cm² (≈33.9 atm). Reaction started approximately 1/2 hr after reaction conditions were attained.

By means of a disk valve, samples of constant volume (5 μl) were taken from the reactor every 10 min for 4–6 hr and introduced into a gas chromatograph. The samples remained under reaction conditions (35 kgf/cm² (≈33.9 atm) and 62°C) until the very moment of expansion and vaporization in the carrier gas stream of the gas chromatograph. Copolymer present in the sample was retained by a precolumn. The peak areas of the three remaining components, ethylene ($A_e$), vinyl acetate ($A_v$), and TBA ($A_b$), were determined by electronic integration of the catharometer signal.

The analytical system was calibrated by injecting, by means of the same sampling device, reference samples of the pure monomers ethylene and
Fig. 1. Simplified scheme of the equipment: (TIC) temperature indicator controller; (PI) pressure indicator; (PIC) pressure (indicator) controller; (FC) flow controller; (A) reactor; (B) compartment for pressure control; (C) sampling device; (D) gas chromatograph; (E) electronic integrator; (F) recorder; (G) digital printer; (H) pressure and flow controllers.

vinyl acetate (relevant peak areas $A_{ae}$ and $A_{av}$) which have well-known densities ($c_{ae}$ and $c_{av}$) under the appropriate conditions.

In this way a number of experiments were carried out for different monomer feed compositions.

**Experimental Data**

To permit computation of the monomer reactivity ratios, the molar feed ratio $q = n_{e}/n_{v}$ ($n_{e}$ and $n_{v}$ are numbers of moles ethylene and vinyl acetate, respectively, in the reactor) and the degree of conversion $f_{v}$ (based on vinyl acetate) were calculated from the measured peak areas for any one sampling. The relations concerned are given by:

$$q = n_{e}/n_{v} = A_{e}A_{v}c_{e}/A_{v}A_{e}c_{v}$$  \hspace{1cm} (1)

and

$$f_{v} = 100 \left\{ 1 - \frac{[A_{v}(A_{b})_{0}/A_{b}(A_{v})_{0}]} \right\}$$  \hspace{1cm} (2)

where the subscript zero denotes the conditions at zero conversion.

**Feed and Product Characteristics**

The total monomer concentration range covered by nine kinetic series lies between 0.91 and 2.85 mole/dm³, while the molar feed ratio $q = n_{e}/n_{v}$
TABLE II
Initiator Concentrations and Some Copolymer Properties for the Various Kinetic Experiments

<table>
<thead>
<tr>
<th>Experimental code</th>
<th>Initiator concentration, mmole/dm³</th>
<th>Ethylene in copolymer, mole-%</th>
<th>osmotic molecular weight</th>
<th>DP</th>
<th>[η] dl/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1.6</td>
<td>19.3</td>
<td>65300</td>
<td>872</td>
<td>0.43</td>
</tr>
<tr>
<td>B</td>
<td>2.4</td>
<td>21.2</td>
<td>55300</td>
<td>749</td>
<td>0.40</td>
</tr>
<tr>
<td>F</td>
<td>1.6</td>
<td>24.3</td>
<td>61000</td>
<td>847</td>
<td>0.42</td>
</tr>
<tr>
<td>E</td>
<td>1.6</td>
<td>28.9</td>
<td>54300</td>
<td>784</td>
<td>0.42</td>
</tr>
<tr>
<td>D</td>
<td>1.6</td>
<td>39.2</td>
<td>38000</td>
<td>600</td>
<td>0.43</td>
</tr>
<tr>
<td>J</td>
<td>2.8</td>
<td>40.0</td>
<td>30700</td>
<td>488</td>
<td>0.42</td>
</tr>
<tr>
<td>II</td>
<td>4.1</td>
<td>55.6</td>
<td>22800</td>
<td>424</td>
<td>0.40</td>
</tr>
<tr>
<td>A</td>
<td>3.3</td>
<td>60.0</td>
<td>22400</td>
<td>438</td>
<td>0.42</td>
</tr>
<tr>
<td>C</td>
<td>2.0</td>
<td>67.5</td>
<td>27600</td>
<td>588</td>
<td>0.45</td>
</tr>
</tbody>
</table>

* $\bar{M}_{os}$ = osmotic molecular weight; DP = average degree of polymerization; [η] = limiting viscosity number at 25°C.

varies between 0.32 and 2.88 (mole fraction ethylene between 0.24 and 0.74). Copolymer concentrations up to 8 wt.-% were reached. The initiator concentrations and some copolymer properties are listed in Table II.

Examination of reaction mixtures revealed that in the relevant region of monomer and copolymer concentrations, no tendency towards phase separation exists.

EVALUATION OF RESULTS

Basic Equation

A generally accepted model describing the free-radical copolymerization was given by Mayo and Lewis and Alfrey and Goldfinger. For any conversion interval 0 – $f_v$ (based on vinyl acetate) the integrated form of their copolymer equation provides an exact relationship given by:

$$f_v - 100 \left[ 1 - \frac{(q/q_0)^{-x_1}}{\left[(x_2q - x_1)/(x_2q_0 - x_1)\right]^{x_1 + x_2 + 1}} \right] = 0 \quad (3)$$

with the molar feed ratio $q = n_e/n_v$, $x_1 = 1/(r_v - 1)$, $x_2 = 1/(r_v - 1)$; the subscript zero indicates the conditions at zero conversion. Equation (3) can be formulated briefly as:

$$F(r_v, q_0, q, f_v) = 0 \quad (4)$$

Feed Compositional Analysis Method

The experimental method described in this paper affords approximately 25 experimental data pairs per high-conversion copolymerization experiment. The substantially increased number of experimental data per kinetic series allows, as compared with the conventional methods, a more pre-
cise evaluation of the monomer reactivity ratios. The computational procedure given here guarantees efficient use of the extended amount of information and will be referred to as the feed compositional analysis (FCA) method.

In the present investigation the experimental data are available, according to eqs. (1) and (2), as a series of values \( q_t = (n_e/n_v)_t \), describing the monomer feed composition at corresponding degrees of conversion \( (f_v)_i \) for any kinetic experiment. Thus each kinetic series \( (k = 1, \ldots, n) \), producing \( g_k \) data pairs \( q_{ik}, (f_v)_{ik} \), yields \( g_k \) conversion intervals \( 0 - (f_v)_{ik} \) and consequently \( g_k \) equations \( F_{ik} \) [cf. eq. (4)]:

\[
F_{ik} = F[r_e, r_v, q_{ik}, (f_v)_{ik}]
\]

where \( i = 1, \ldots, g_k \) and \( g_k \) is the number of input data pairs resulting from the \( k \)th experiment; \( k = 1, \ldots, n \) and \( n \) is the number of kinetic series.

![Confidence regions derived from the FCA method](image)

**Fig. 2.** Confidence regions, derived from the FCA method; \( r_e \) (ethylene) and \( r_v \) (vinyl acetate) are the monomer reactivity ratios, \( \hat{r}_e \) and \( \hat{r}_v \) are the least-squares estimates of \( r_e \) and \( r_v \), and \( \alpha \) denotes probability level.
According to eqs. (3) and (4) $F_{ik}$ represents the difference between the measured degree of conversion ($f_v$) and the corresponding calculated expression for the degree of conversion; ($q_{0k}$ is the intercept on the $q$ axis of the $q$ versus $f_v$ relations of which an example is given in Figure 3). Owing to the random experimental error, generally $F_{ik} \neq 0$ for any $r_e$, $r_v$, and $q_{0k}$ combination. Now, the combined information resulting from all kinetic experiments (221 data pairs) gives ample information to determine the least-squares estimates for $r_e$, $r_v$, and $q_{0k}$ by selecting those values of $r_e$, $r_v$, and $q_{0k}$ that minimize:

$$\sum_{k=1}^{n} \sum_{i=1}^{q_k} F_{ik}^2 \left[ r_e, r_v, q_{0k}, q_{ik}, (f_v)_{ik} \right]$$

For the solution of this nonlinear least-squares method, a computer program in Algol 60 is available upon request.

RESULTS

The above minimization procedure immediately leads to the least-squares estimates for $r_e$, $r_v$, and $q_{0k}$; also the standard deviations can be calculated:\textsuperscript{11}  

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

However, the joint confidence limits which are shown in Figure 2 are to be given preference over these perpendicular confidence intervals, since only the former indicate which pairs of $r_e$, $r_v$ values are consistent with the input data.
In order to ascertain the consistency of the Mayo-Alfrey model with the experimental data, the relations between the molar feed ratio \( q = n_e/n_v \) and the degree of conversion \( f_v \) are recomputed for all experiments with \( f_e = 0.743 \) and \( f_v = 1.515 \). A representative example for experiment J is given in Figure 3.

The adequacy of the model has been proved by statistically comparing the error pattern derived from the curve-fitting procedure with the experimental error of the input data. It may be concluded that the Mayo-Alfrey model is completely supported by the data obtained under the relevant conditions within the narrow limits imposed by the experimental error.

**CONCLUSIONS**

The product of the reactivity ratios \( r_e r_v = 1.12 \), being larger than unity, indicates that the copolymers concerned are distributed in a somewhat blockier fashion than the random distribution would predict.

The adequacy of the Mayo-Alfrey model implies that \( r_e \) and \( r_v \) are independent of the monomer feed composition, the copolymer concentration,
and the degree of polymerization. Although from the theoretical point of view the best measure of reactivity is in units of mole/dm$^3$, it is surprising that this activity measure holds over such a large region of monomer and copolymer concentrations.

While penultimate effects are evidently negligible, the literature and our own measurements indicate the occurrence of anomalous additions. However, these do not disturb the model fit in the present case.

The relevant $r$ values and consequently the feed-product relationship at low pressure, given in Figure 4, are significantly different from the published results at higher pressures. In addition to influencing reaction rate constants, pressure may have caused the latter results to be severely biased by phase separation.

Even at pressures as low as 35 kgf/cm$^2$ (= 33.9 atm), in the liquid phase at 62°C and with free-radical initiation, high molecular weight copolymers of ethylene and vinyl acetate can be prepared over a wide composition range.

References


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