Copolymerization of Vinyl Acetate with a Homologous Series of Vinyl Esters: A Comparative Study of Vinyl Acetate-Vinyl Ester and Ethylene-Vinyl Ester Copolymerization

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Synopsis

The effect of the alkyl group on the relative reactivity of a homologous series of vinyl esters \([M_2]\) has been studied with vinyl acetate \([M_1]\) as reference monomer and tert-butyl alcohol as solvent at 62°C and 35 kg/cm\(^2\). The description of the relative reactivities of the vinyl esters toward the vinyl acetate (VAc) macroradical in terms of the Taft relation is analogous to our previous findings in a similar study with ethylene (Eth) as reference radical. This implies that chiefly polar factors affect the relative reactivity, whereas from vinyl pivalate (VPV) on steric hindrance impairs the addition rate. The constancy of the \(r_2\) values, also found in the series with Eth \([M_1]\) as reference monomer \((\text{viz., } r_2 = 1.50)\), appears to exist in the present investigation \((r_2 = 1.04)\) but does not hold for the VAc-VPV combination. This can be interpreted in terms of steric hindrance. A combination of kinetic results indicates sterically hindered additions in all those reactions in the system Eth-VAc-VPV that involve at least one VPV unit as macroradical or monomer (except for the addition of Eth to a VPV macroradical). The monomer reactivity ratios that pertain to the Eth-VAc-vinyl ester systems are discussed in terms of the \(Q-e\) scheme and the product relation postulated by Ham. The Ham relation does not hold for the latter systems.

INTRODUCTION

In an earlier study\(^1\) the correlation between reactivity and monomer structure for a homologous series of esters derived from vinyl alcohol was investigated with ethylene as reference monomer. Interpretation in terms of the well-known Taft relation\(^2\) showed that the relative reactivities of the vinyl esters were affected mainly by polar factors. The relative reactivities appeared to increase with the decreasing electron-withdrawing ability of the ester side group,\(^1\) which was found to be in qualitative agreement with similar studies on homologous series of vinyl esters toward \(N\)-vinylcarbazole,\(^3\) methyl methacrylate,\(^4,5\) and styrene\(^4\) as reference monomers, respectively. On the other hand, a reversed relative reactivity of the vinyl esters was observed toward chloroprene\(^6\) and vinyl chloride\(^7\) macroradicals. From these separate investigations, however, it was impossible to decide whether the observed differences should be attributed to the differing nature of the various reference radicals or to the noncorresponding experimental conditions.

This article aims primarily at a comparison of the trend of the relative reactivities of homologs in a series of vinyl esters toward two different reference radicals; that is, ethylene\(^1\) and vinyl acetate.

Furthermore, the combined present and earlier results permit us to check the validity of Ham’s product relation of $r$ values:

$$r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21}, \quad r_{ij} = k_{ii}/k_{ij}$$

(1)

for the systems $M_1$ = ethylene, $M_2$ = vinyl acetate, $M_3$ = vinyl propionate, vinyl butyrate, vinyl isobutyrate, and vinyl pivalate.

**HAM RELATION**

The Ham relation, given by eq. (1), can be derived directly from the postulated relationship of product probabilities, which is actually based on the assumption that the overall probability of initiating $M_2$, $M_3$, and $M_1$ sequences, preceded by $M_1$, $M_2$, and $M_3$, successively, is equal to the probability of terminating the same sequences with $M_1$, $M_2$, and $M_3$ units:

$$p_{12}p_{23}p_{31} = p_{13}p_{32}p_{21} = \mathcal{P}$$

(2)

where, for example,

$$p_{12} = k_{12}[^{\sim}M_1][M_2]/(k_{11}[^{\sim}M_1][M_1] + k_{12}[^{\sim}M_1][M_2] + k_{13}[^{\sim}M_1][M_3])$$

(3)

is the probability of the occurrence of the reaction $[^{\sim}M_1] + M_2$ in the ternary system $M_1 - M_2 - M_3$ in relation to all possible additions to the $[^{\sim}M_1]$ radical. According to Ham, $\mathcal{P}$ is a characteristic constant, depending on the ternary system under consideration; for instance, for three conjugated or three unconjugated monomers this constant would assume the value $\mathcal{P} = 0.037$.

An interesting aspect of the Ham relation [eq. (1)] is that it directly follows from the $Q-e$ scheme applied to a ternary system of monomers. Ham found that eq. (1) was valid for a number of ternary systems. His selection, however, of $r$ values from the literature was questioned and remains debatable. Mayo opposed not only the agreement of eq. (1) with the experimental data cited but its theoretical foundation as well and finally recast eq. (1) as

$$H = \frac{r_{12}r_{23}r_{31}}{r_{13}r_{32}r_{21}}$$

(4)

where the $H$ factor enables the extent of consistency of Ham’s hypothesis to be checked. The poorer the agreement between theory and experiment, the more $H$ will deviate from unity. Mayo did not rule out the existence of certain patterns in the deviations of $H$ from unity.

**EXPERIMENTAL**

The quality of the monomers vinyl acetate (VAc), vinyl propionate (VP), vinyl butyrate (VB), vinyl isobutyrate (VIB), and vinyl pivalate (VPV), the solvent tert-butyl alcohol (TBA), and the free radical initiator $\alpha,\alpha'$-azobisisobutyronitrile (AIBN) is identical to that reported previously. The free radical copolymerization reactions have been carried out under the experimental conditions reported earlier for ethylene (Eth)–vinyl ester copolymerizations; that is, 62 ± 0.1°C, 35 kg/cm² with TBA as solvent and AIBN as initiator. The experimental methods, based on quantitative gas–liquid chromatographic (GLC) analysis of
the reaction mixture throughout the copolymerization, has been described elsewhere. The details of the various kinetic experiments for each binary system considered are summarized in Table I.

The monomer reactivity ratios have been evaluated by the recently described (improved) curve-fitting procedure, which takes into account relative measurement errors in the GLC peak areas of VAc (M1), vinyl ester (M2), and the solvent of 1.0, 1.0, and 1.5%, respectively, independent of the degree of conversion to copolymer.

RESULTS AND DISCUSSION

Examination of the calculated reactivity ratios of the VAc (M1)–vinyl ester (M2) copolymerizations, summarized in Table II, and their confidence regions shown in Figure 1 reveals a coincidence within experimental error of the systems VAc–VP and VAc–VB. For the VAc–VIB binary combination \( r_1 \) is significantly

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### Table I

Experimental Conditions of the Copolymerizations of Vinyl Acetate (M1) with Various Vinyl Esters (M2)

<table>
<thead>
<tr>
<th>Vinyl ester (M2)</th>
<th>Initial monomer feed ratio ( q_0 )</th>
<th>Final monomer feed ratio ( q_f )</th>
<th>Conversion based on M1 (%)</th>
<th>Number of observations</th>
<th>Initiator concentration (mmole/dm³)</th>
<th>Total initial monomer concentration (mole/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl butyrate</td>
<td>3.9678</td>
<td>4.2785</td>
<td>59.12</td>
<td>27</td>
<td>3.1</td>
<td>1.51</td>
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<tr>
<td></td>
<td>2.3394</td>
<td>2.4278</td>
<td>39.86</td>
<td>24</td>
<td>3.1</td>
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<td></td>
<td>1.5607</td>
<td>1.5653</td>
<td>40.48</td>
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<td></td>
<td>1.0614</td>
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<td>36.63</td>
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<td>1.50</td>
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<td>0.6526</td>
<td>0.6815</td>
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<td></td>
<td>0.4006</td>
<td>0.4092</td>
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<td></td>
<td>0.2529</td>
<td>0.2585</td>
<td>40.77</td>
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<td>4.2</td>
<td>1.50</td>
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<td>Vinyl isobutyrate</td>
<td>4.0762</td>
<td>4.3721</td>
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<td>20.77</td>
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<td>1.6</td>
<td>1.20</td>
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<tr>
<td>Vinyl pivalate</td>
<td>3.9007</td>
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<td>39.93</td>
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<td>1.0538</td>
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<td>1.4</td>
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<td>0.8854</td>
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<td>0.4290</td>
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<td>0.2930</td>
<td>0.3114</td>
<td>34.79</td>
<td>21</td>
<td>1.3</td>
<td>1.03</td>
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</table>

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*a* For vinyl propionate the conditions have been reported elsewhere. b Calculated from the best-fitting curves resulting from the curve-fitting I-intersection procedure that takes into account the error structure of the primary experimental data (cf. ref. 15).
<table>
<thead>
<tr>
<th>Vinyl ester (Mz)</th>
<th>r₁</th>
<th>r₂</th>
<th>( \pi = r₁ - r₂ )</th>
<th>( e₁ )</th>
<th>( e₂ )</th>
<th>Ethylene as reference monomer</th>
<th>Vinyl acetate as reference monomer</th>
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<tr>
<td>VAcb</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.026</td>
<td>-0.22</td>
<td>0.026</td>
<td>-0.22</td>
</tr>
<tr>
<td>VP</td>
<td>0.90 ± 0.03</td>
<td>0.93</td>
<td>0.07</td>
<td>-0.49</td>
<td>-0.49</td>
<td>0.027</td>
<td>-0.20</td>
</tr>
<tr>
<td>VB</td>
<td>0.90 ± 0.007</td>
<td>0.83</td>
<td>0.07</td>
<td>-0.49</td>
<td>-0.49</td>
<td>0.027</td>
<td>-0.20</td>
</tr>
<tr>
<td>VIB</td>
<td>0.81 ± 0.02</td>
<td>0.85</td>
<td>0.02</td>
<td>-0.51</td>
<td>-0.51</td>
<td>0.027</td>
<td>-0.20</td>
</tr>
<tr>
<td>VVP</td>
<td>0.88 ± 0.02</td>
<td>1.03</td>
<td>1.03</td>
<td>0.030</td>
<td>0.030</td>
<td>0.029</td>
<td>0.030</td>
</tr>
</tbody>
</table>

*Assuming for vinyl acetate: \( Q₁ = 0.026 \) and \( e₁ = -0.22 \).

Hypothetical copolymerization.

Estimated standard deviations.

Assuming that \( r₁ = r₂ = 1.00 \).
smaller than for the VAc–VP and VAc–VB combinations, which indicates primarily that the vinyl ester reactivity increases with the decreasing electron-withdrawing character of the ester side group. The observed reactivity of VPV showed a deviating behavior, which is explained later on.

Application of the $Q-e$ scheme of Alfrey and Price$^{16}$ to the present results leads to almost identical and invariably small $Q$ values for all the vinyl esters considered (Table II). Moreover, the present $Q$ values do not deviate significantly from values determined for Eth–vinyl ester copolymerizations.$^1$

The present $e$ values of the vinyl esters show a tendency to become increasingly negative, as the ester side group becomes less electron withdrawing, analogous to the values resulting from the Eth–vinyl ester copolymerizations.$^1$ However, the $e$ values of the vinyl esters that result from the present VAc–vinyl ester copolymerizations differ considerably from those obtained from the Eth–vinyl ester copolymerizations.$^1$ This suggests that for any binary combination of Eth, VAc, and vinyl ester the $Q-e$ scheme will hardly help to interpret and predict $r$ values. The more so as it allows only those products of $r$ values, $\pi$, that are smaller than or equal to unity. This condition is not fulfilled for a number of binary combinations. Especially important in this respect is the fact that for the combination of the two reference monomers, namely, the Eth–VAc combination, the $\pi$ value exceeds unity rather strongly$^{1,13}$: $\pi = 1.11$.

The Ham relation$^8-10$ may still constitute a more useful scheme for the prediction of $r$ values than the $Q-e$ scheme. Because rejection of the $Q-e$ scheme does not necessarily imply the failure of the Ham relation, the applicability of the Ham concept has been tested for the combined data from the Eth–vinyl ester$^1$ and the VAc–vinyl ester copolymerizations. The calculated $H$ factors, defined by eq. (4), for the Eth ($M_1$)–VAc ($M_2$)–vinyl ester ($M_3$) systems are given in Table III. Although in view of the magnitude of their standard deviations no decisive conclusion with regard to a possible drift of the $H$ factors can be drawn, the conclusion that the $H$ factors in Table III are systematically somewhat below unity appears to be justified. This indicates that, at least for the present systems, the Ham relation, as given in eq. (1), does not hold. Nevertheless, the $H$ constant,
which in the first instance indicates the extent of the validity of Ham’s theory, may have a deeper physical meaning. Therefore knowledge of the $H$ constants for a wider variety of systems may help toward a better interpretation and more accurate prediction of the $r$ values of uninvestigated binary combinations. The average $P$ value for the present systems (0.035) is close to the value theoretically predicted by Ham: $P = 0.037$. A value of $P = (1/3)^3 = 0.037$ would occur when the average value $p_{ij} = 1/3$; that is, a special case of “ideal terpolymerization,” in which the overall probability of initiating $M_2, M_3$, and $M_1$ sequences preceded by $M_1, M_2$, and $M_3$ would indeed be equal to the probability of terminating the same sequences with $M_1, M_2$, and $M_3$, respectively. Although it is plausible that in the present case this situation may be approximated, the variations in the probability products in Table III indicate that in detail Ham’s theory is not supported by relevant results.

A description of the relevant copolymerization behavior according to the $Q-e$ scheme appears to be unsatisfactory. Because resonance stabilization within the homologous series of vinyl esters is of minor importance (almost constant $Q$ values), it is worthwhile to try to correlate the observed $r$ values by means of another two-parameter model that accounts for steric hindrance instead of resonance stabilization; for example, the well-known Taft relation:

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

in which $1/r_1 = k_{12}/k_{11}$ represents the reactivity of the vinyl ester monomer ($M_2$) in relation to the VAc monomer ($M_1$), toward a radical chain end with an ultimate VAc unit; $\sigma^*$ and $E_s$ are Taft’s polar and steric constant, respectively, and $\rho^*$ and $\delta$ are the respective reaction constants that show to what extent polar and steric effects contribute. It then becomes possible to decide whether the relative reactivity of a homologous series of monomers is affected by polar factors, steric factors, or both. Figure 2 shows a linear relationship of $\log(1/r_1)$ versus the polar substituent constant $\sigma^*$ for the various VAc ($M_1$)–vinyl ester ($M_2$) copolymerizations. (Observation 1 in Fig. 2 refers to the hypothetical VAc–VAc copolymerization, where $r_1 = r_2 = 1$.) For VPV, however, a reactivity toward the VAc macroradical is observed, which is significantly lower than would be expected, considering its polar reaction constant only. Both the resulting polar reaction constant $\rho^* = -0.47$ and the steric reaction constant $\delta = 0.05$ for VPV only [$E_s = 0$ for $-\text{CH}_3$ and $E_s = -1.55$ for $-\text{C(CH}_3)_3$] appear to be equal within experimental error to the values that can be derived from our previous findings for

\[
\begin{array}{ccccccc}
\text{Vinyl ester} & Y = r_{12}r_{23}r_{31} & Z = r_{13}r_{32}r_{21} & H = Y/Z & p_{12}p_{23}p_{31}^a & p_{13}p_{32}p_{21}^a \\
(M_2) & & & & & \\
VP & 1.00 & 1.04 & 0.96 \pm 0.09^b & 0.0356 & 0.0342 \\
VB & 1.00 & 1.08 & 0.92 \pm 0.05 & 0.0361 & 0.0334 \\
VIB & 0.89 & 0.96 & 0.93 \pm 0.09 & 0.0368 & 0.0343 \\
VPV & 0.97 & 1.13 & 0.85 \pm 0.07 & 0.0373 & 0.0320 \\
\end{array}
\]

* Assuming equimolar monomer concentrations in the feed.
  
  b Estimated standard deviations.
Copolymerization of Vinyl Acetate 3371

10.1-
I--
0.0-
0.29
0.35
Fig. 2. Relation between log(1/r1) and −σ* for the copolymerizations of vinyl acetate (M1) with a homologous series of vinyl esters: vinyl acetate (obs. 1), vinyl propionate (2), vinyl butyrate (3), vinyl isobutyrate (4), and vinyl pivalate (5).

corresponding copolymerizations of the same series of vinyl esters toward Eth as reference monomer: ρ* = −0.42 and δ = 0.04. From these results it may be concluded that the Eth and VAc macroradicals exhibit a similar steering effect on the vinyl ester monomer reactivity. On the other hand, strongly varying and deviating values of ρ* are given in the literature for the copolymerization of the present homologous series toward various other reference monomers. Although ρ* values in those cases will be affected by the character of the reference radical, the varying nature of the reaction medium may play an important part as well.

In this context our recent study of the effect of solvent in the free radical Eth–VAc copolymerization17 becomes of paramount importance. The results of this study have shown a significant effect of solvent on both r values, which indicates a solvent-dependent VAc monomer reactivity.

The surprising constancy of the previously determined r2 values for Eth (M1)–vinyl ester (M2) copolymerizations1 is also revealed within the present series of VAc (M1)–vinyl ester (M2) copolymerizations, except for the VAc–VPV binary combination, where r2 is substantially higher than the values observed for the three other systems (Table II). The phenomenon of constancy of the r2 values could be caused by the usually dominating contribution of the radical reactivity to the chain propagation rate constants,18,19 which obscures the relatively small differences among the vinyl ester monomer reactivities.

Table IV is a survey of the combined results obtained so far on sterically hindered propagations within the system Eth–VAc–VPV. Four addition reactions

<table>
<thead>
<tr>
<th>Table IV</th>
<th>Survey of the Sterically Hindered Propagations (+) Within the System Ethylene (Eth)–Vinyl Acetate (VAc)–Vinyl Pivalate (VPV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radicals</td>
<td>Ethiso(−M1)</td>
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<tr>
<td>Eth (M1)</td>
<td>-</td>
</tr>
<tr>
<td>VAc (M2)</td>
<td>-</td>
</tr>
<tr>
<td>VPV (M3)</td>
<td>+</td>
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</table>
appear to be impaired by steric hindrance. In a previous investigation\(^1\) and in the present article it has been clearly demonstrated that the addition of VPV to the Eth and VAc macroradicals is impeded, whereas the addition reactions \(\sim\text{Eth}^+ + \text{VAc}\) and \(\sim\text{VAc}^- + \text{VAc}\), and as a consequence \(\sim\text{Eth}^+ + \text{Eth}\) and \(\sim\text{VAc}^- + \text{Eth}\), were not affected by steric hindrance. These findings necessarily imply that the addition of the VPV monomer to its own macroradical is also impeded. The ratio of the addition rates of the chain propagation reactions \(\sim\text{VPV}^- (3) + \text{VAc} (2)\) and \(\sim\text{VPV}^- (3) + \text{Eth} (1)\) appears to be substantially lower \((k_{32}/k_{31} = 1.50/1.17 = 1.28)\) than the corresponding reactions of VAc (2) and Eth (1) to the other relevant vinyl ester (3) macroradicals \((k_{32}/k_{31} = r_{31}/r_{32} = 1.50/1.04 = 1.44)\) (cf. ref. 1 and Table II). This indicates that the \(\sim\text{VPV}^- (3) + \text{VAc} (2)\) addition reaction \((k_{32})\) is probably retarded by steric hindrance, whereas the \(\sim\text{VPV}^- (3) + \text{Eth} (1)\) addition reaction \((k_{31})\) is impaired to a lesser extent or not at all. A study\(^2\) of the effect of pressure on copolymerizations in the system Eth–VAc–VPV will also indicate the absence of steric hindrance in the \(\sim\text{VPV}^- + \text{Eth}\) addition. The possibility, however, of some steric hindrance in the latter reaction basically still exists.

The results of Nozakura et al.\(^2\) may provide further supporting evidence of the present conclusions because they reported an enhanced preference for syndiotactic over isotactic triads in free radical addition reactions of vinyl ester homopolymerization, starting from VIB.

The most striking fact in Table IV is that the Eth addition to the VPV radical seems not to be retarded, whereas all other addition reactions involving a VPV monomer or a VPV radical, including the addition of the VPV monomer to the Eth macroradical, appear to be impaired by steric hindrance. Primarily, this suggests that the pivalate side group of the VPV monomer is shielding the vinyl group. Depending on the way of approach required, this may result in a hampered addition of the VPV monomer to any macroradical. Apparently the absence of a side group in Eth allows an approach to any radical species without steric hindrance.

On the other hand, a more critical situation should be expected in the attack of a VPV macroradical on any monomeric species. However, the pivalate side group of the VPV radical, although present on the terminal C atom, does not seem to shield the free electron orbital because the addition reaction of \(\sim\text{VPV}^- + \text{Eth}\) is most probably not impeded. As for the attack of the VPV macroradical on VAc, the geometry in the transition state of both species appears to be decisive for the occurrence of steric hindrance. This addition reaction will have a lower activation energy if the side groups of radical and monomer in the transition state are in the syndiotactic position.

$\text{CONCLUSIONS}$

The relative reactivity of the present vinyl ester homologs toward the VAc macroradical increases as the electron-withdrawing effect of the ester side group decreases, thus indicating that the relative reactivity is mainly affected by polar terms. Resonance stabilization plays a minor part in relative reactivity, but a significant steric effect shows up in the VPV addition to the VAc radical chain end. In terms of the Taft relation\(^2\) the resulting polar reaction constant, as well as the steric reaction constant for VPV only, appears to be almost equal to the
values derived from our previous results concerning the copolymerization of the same series of vinyl esters toward Eth as reference monomer.

The constancy of the \( r_2 \) values (except for Vac–VPV), also observed in our earlier study, is indicative of the dominating influence of the nature of the reference radical on the reactivity in chain propagation.

Further combination of the present results with those obtained earlier reveals the occurrence of steric hindrance in those propagation reactions within the system Eth–VAc–VPV that involve at least one VPV unit as monomer or macroradical. The Eth addition to the VPV macroradical forms an exception in this respect. The present findings suggest shielding of the vinyl moiety by the pivalate side group in the VPV monomer.

As might be anticipated on the basis of the present results, neither the \( Q-e \) scheme nor the Ham relation has been found to be suitable for the description and prediction of \( r \) values pertaining to the system Eth—VAc—vinyl esters.

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References