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# Remote Unit Effects in the Copolymerization of Unconjugated Monomers

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# Remote Unit Effects in the Copolymerization of Unconjugated Monomers

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## SUMMARY

The kinetics of the radical copolymerization of the three binary systems vinyl chloride (C)–vinyl acetate (Ac), vinylidene chloride (V)–vinyl acetate, and vinyl chloride–vinylidene chloride have been investigated in the whole range of monomer feed composition using the chromatographic method. Penultimate or antepenultimate effects have been observed in all cases. The better values of the corresponding reactivity ratios are: For C-Ac copolymers, $r_{Ac} = 0.29$, $r_{CCC} = 1.67$, $r_{AcCC} = 4.60$, and $r_{AcC} = 2.05$. For V-Ac copolymers, $r_{Ac} = 0.07$, $r_{VVV} = 5.30$, $r_{AcVV} = 11.5$, $r_{AcAcV} = 8.0$, and $r_{VAcV} = 6.0$. For C-V copolymers, $r_C = 0.22$, $r_{VV} = 2.94$, and $r_{CV} = 4.31$. An internal transfer mechanism is suggested for the antepenultimate effect in the vinyl acetate copolymers.

## INTRODUCTION

In the preceding paper [1] it has been shown that in the copolymerization of vinyl chloride, which is an unconjugated monomer, with one conjugated monomer, namely acrylonitrile, methyl methacrylate, or styrene, penultimate effects were always observed and were the most important for the vinyl chloride ended radicals. Thus, a conjugated monomer penultimate unit strongly changes the reactivity of the unconjugated chain end radical. The changes are possibly related to the polarity of the conjugated monomers. The reverse is not true, and a vinyl chloride unit does not affect the reactivity of a methyl methacrylate ended radical; its effect is weak on an acrylonitrile-ended radical and is more important, but of another kind (antepenultimate) in the case of a styrene-ended radical. We thought it interesting to try to obtain more knowledge about the possible type of remote-units effects in the copolymerization of unconjugated monomers. Ethylene is a typical unconjugated monomer without steric or polarity effects, but it may be copolymerized with either vinyl chloride or vinyl acetate. The study of sequence distributions by high resolution NMR techniques led Schaefer [2] to conclude remote-unit effects were absent in both cases. This was confirmed by Wilkes et al. [3] for the ethylene–vinyl chloride copolymers. However, these investigations did not cover the extreme ranges of the copolymer composition.

Our study has been limited to the three most available unconjugated monomers: vinyl chloride (C), vinylidene chloride (V), and vinyl acetate (Ac). In all cases significant remote-unit effects have been observed and their origin is discussed. The three binary copolymerizations involved have been thoroughly described in the literature and the data of several authors agree quite well. (The results are reported in Table 1.) Until now, however, the penultimate and antepenultimate effects have never been reported.

## II. EXPERIMENTAL RESULTS

The binary copolymerizations were carried out at 60°C in about 20 wt % solution in either dimethylformamide (DMF), tetrahydrofurane (THF), or cyclohexanone, azodiisobutyronitrile being the initiator. Monomers and solvents (commercial grade) were freshly distilled before use under a dry nitrogen atmosphere. Kinetic studies were by the chromatographic method previously described [18]. The initial charges and kinetic results are reported in Tables 2, 3, and 4, respectively, for the systems C-Ac, V-Ac, and V-C.

### A. Vinyl Chloride (C)–Vinyl Acetate (Ac) Copolymerization

Precipitation of these copolymers was somewhat difficult. Several nonsolvents were used (methanol–water mixture, water), but NMR analysis showed no significant compositional drift between fractions collected from the same copolymer.

**Table 1.** Literature Data for the Three Binary Copolymerization of Vinyl Chloride (C), Vinylidene Chloride (V), and Vinyl Acetate (Ac)

| Monomers A | B | Data $r_A$ | $r_B$ | T (°C) | Experimental conditions | Number of experiments | Range, $x_A = A/B$ | Copolymer analysis | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Ac | C | 0.23 | 1.68 | 60 | Bulk | 4 | 0.3-3.4 | Cl | 4 |
| Ac | C | 0.30 | 2.45 | 60 | Bulk | 5 | 0.3-34 | NMR | 5 |
| Ac | C | 0.30 | 2.10 | 68 | Bulk | 4 | | Cl | 6 |
| Ac | C | 0.28 | 2.0 | 60 | Bulk | 7 | 0.17-6.9 | Cl | 7 |
| Ac | C | 0.60 | 1.8 | 40 | Bulk | | | Chemical | 8 |
| V | C | 3.15 | 0.23 | 55 | Bulk | 16 | 0.013-5.8 | Cl | 9 |
| V | C | 3.20 | 0.30 | | | | | Cl | 10 |
| V | C | Large | 0.14 | 68 | Bulk | | | Cl | 6 |
| V | C | 4.5 | 0.20 | 50 | Bulk | | | | 11 |
| V | C | 3.2 | 0.20 | 50 | Bulk | 14 | 0.05-10 | IR | 12 |
| V | C | 4.5 | 0.16 | 50 | Suspension | 4 | 0.16-2.6 | NMR | 13 |
| Ac | V | 0.05 | 5.0 | 50 | – | 10 | 0.25-13.3 | – | 14 |
| Ac | V | 0.05 | 6.70 | 60 | Bulk | 6 | | NMR | 15 |
| Ac | V | 0.10 | 6.00 | – | Bulk | – | | Cl | 6 |
| Ac | V | 0 | 3.60 | 60 | Bulk | 4 | 0.27-2.5 | Cl | 16 |
| Ac | V | 0.05 | 6.70 | 60 | Bulk | 6 | 0.9-19 | NMR | 17 |

**Table 2.** Charges and Kinetic Results in the Copolymerization of Vinyl Chloride (C) and Vinyl Acetate (Ac)

| C (moles) | Ac (moles) | Solvent DMF (moles) | $x_C = \frac{C}{Ac}$ | $n_C = \frac{d_C}{d_{Ac}}$ |
|---|---|---|---|---|
| 0.018 | 0.593 | 5.48 | 0.032 | 0.104 |
| 0.278 | 0.617 | 6.02 | 0.450 | 1.22 |
| 0.288 | 0.275 | 5.85 | 1.047 | 2.455 |
| 0.736 | 0.342 | 5.50 | 2.15 | 4.70 |
| 1.055 | 0.2343 | 5.56 | 4.50 | 7.50 |
| 0.820 | 0.0916 | 5.85 | 8.95 | 16.25 |
| 0.812 | 0.055 | 5.63 | 14.65 | 25.80 |
| 0.733 | 0.0210 | 5.06 | 33.50 | 57.0 |
| 0.815 | 0.019 | 5.50 | 42.90 | 64.0 |

**Table 3.** Charges and Kinetic Results in the Copolymerization of Vinylidene Chloride (V) and Vinyl Acetate (Ac)

| V (moles) | Ac (moles) | Solvent DMF (moles) | $x_V = \frac{V}{Ac}$ | $n_V = \frac{d_V}{d_{Ac}}$ |
|---|---|---|---|---|
| 0.00970 | 0.692 | 5.36 | 0.0138 | 0.175 |
| 0.0258 | 0.675 | 5.12 | 0.0382 | 0.388 |
| 0.0412 | 0.705 | 5.44 | 0.0585 | 0.660 |
| 0.0784 | 0.714 | 5.48 | 0.1095 | 0.980 |
| 0.115 | 0.535 | 5.43 | 0.215 | 1.85 |
| 0.73 | 0.207 | 5.50 | 3.54 | 20.90 |
| 0.722 | 0.0745 | 5.43 | 9.76 | 63.50 |
| 0.381 | 0.027 | 5.25 | 14.05 | 77.20 |
| 0.740 | 0.0425 | 4.25[a] | 17.40 | 94.20 |
| 0.660 | 0.0245 | 4.08[a] | 26.90 | 119 |
| 0.0571 | 0.0132 | 4.11[a] | 43.10 | 181 |

[a] Solvent: cyclohexanone.

**Table 4.** Charges and Kinetic Results in the Copolymerization of Vinyl Chloride (C) and Vinylidene Chloride (V)

| V (moles) | C (moles) | Solvent THF (moles) | $x_V = \frac{V}{C}$ | $n_V = \frac{d_V}{d_C}$ |
|---|---|---|---|---|
| 0.529 | 0.0141 | 5.11 | 37.2 | 113.5 |
| 0.750 | 0.0438 | 5.06 | 17.50 | 50.70 |
| 0.542 | 0.0512 | 5.60 | 10.58 | 25.30 |
| 0.650 | 0.224 | 5.28 | 2.900 | 8.90 |
| | | 4.96 | 1.81 | |
| 0.157 | 0.277 | 3.85 | 0.567 | 2.18 |
| 0.063 | 0.566 | 5.22 | 0.111 | 0.466 |
| 0.505 | 0.957 | 5.27 | 0.0527 | 0.210 |
| 0.0199 | 0.892 | 5.45 | 0.020 | 0.090 |

The Fineman-Ross [19] plot of the experimental results $(n_C - 1)/x_C$ vs. $n_C/x_C^2$ is illustrated in Fig. 1. It gives a straight line which take account of the results for the major part of the monomer feed range. The corresponding reactivity ratios are $r_C = 2.01 \pm 0.16$ and $r_{Ac} = 0.29 \pm 0.02$, in good agreement with several literature values [5-7].

A departure from the straight line is observed for the mixture rich in vinyl chloride ($x_C > 10$), indicative of a penultimate effect. Given the value of $r_{Ac}$, application of the procedure described by Barb [20] yields $r_{CC} = 1.80$ and $r_{AcC} = 2.20$. However, the Barb equation with the above values does not fit all the experimental points and an antepenultimate effect is indicated for $x_C > 15$.

In the other extremity of the composition range, the Fineman-Ross straight line fits all the experimental points up to $x_{Ac} = 30$ well. Thus, there are no remote-unit effects on the vinyl acetate-ended radicals. In order to obtain the values of the four reactivity ratios corresponding to the antepenultimate effects on the vinyl chloride-ended radicals, the following procedure has been used, based on the Ham equation [21]

$$n = \frac{1 + \left[\frac{r_1'''x(r_1''x + 1)}{r_1'''x + 1}\right]\left[\frac{r_1'x(r_1x + 1)}{r_1'x + 1} + 1\right] \Big/ \left[\frac{r_1'''x(r_1''x + 1)}{r_1'''x + 1} + 1\right]}{1 + \frac{r_2'''}{x}\left(\frac{r_2'' + x}{r_2''' + x}\right)\left[\frac{r_2'[(r_2 + x)/(r_2' + x)] + x}{r_2'''[(r_2'' + x)/(r_2''' + x)] + x}\right]} \qquad (1)$$

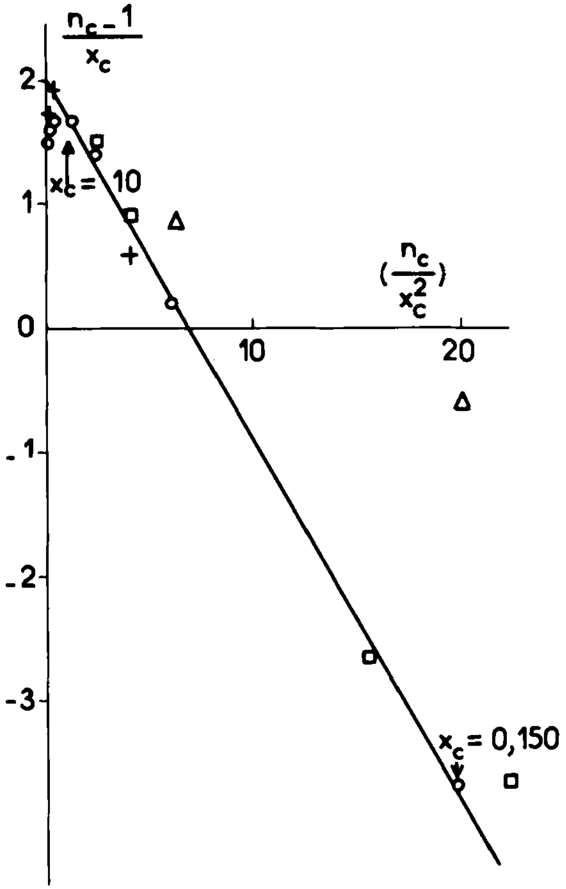


Fig. 1. Vinyl chloride (C)–vinyl acetate (Ac) copolymerization, Fineman-Ross plot. (+) Agron et al. [6]; (□) Hayashi and Otsu [7]; (△) Grassie et al. [5]; and (○) this study.

(It is noteworthy that the denominator is equal to $1 + r_{Ac}/x$, as no remote unit effect is observed in this case on vinyl acetate-ended radical.) First, only great values of x are considered since in this range of monomer feeds the influence of $r_{CAcC}(r_1')$ and $r_{AcAcC}(r_1'')$ is negligible on the kinetics; it is then possible to assume, in a first step of calculation, that $r_{AcAcC} = r_{CAcC} = r_{AcC} = 2.20$.

Equation (1) may be written

$$n_C = \frac{1 + \left[\dfrac{r_{AcC}x_c}{r_{AcC}x_c + 1}\right]\left[1 + \dfrac{r_{AcCC}x_c(r_{CCC}x_c + 1)}{r_{AcCC}x_c + 1}\right]}{1 + r_{Ac}/x_c} \qquad (2)$$

Given the value of $r_{Ac} = 0.29$, Eq. (2) involves only two unknown reactivity ratios: $r_{CCC}(r_1)$ and $r_{AcCC}(r_1')$.

A linearization procedure yields

$$P = (1/r_{CCC}r_{AcCC}) + (1/r_{CCC})\,Q$$

with

$$P = \frac{r_{AcC}x_c^2}{(N_c - 1)(r_{AcC}x_c + 1) - r_{AcC}x_c}\,x_c$$

$$Q = x_c - \frac{r_{AcC}x_c^2}{(N_c - 1)(1 + r_{AcC}x_c) - r_{AcC}x_c} \quad \ldots$$

and $N_c = n_c(1 + r_{Ac}/x_c)$.

A plot of P vs. Q is given in Fig. 2; from which $r_{AcCC} = 2.30$ and $r_{CCC} = 1.67$ are obtained. Then, in order to take into account the results of the intermediate composition range, the Ham equation is reused, given $r_{Ac}$, $r_{AcCC}$, and $r_{CCC}$, and permits better values of $r_{AcAcC}$ and $r_{CAcC}$ to be obtained. A similar procedure leads to

$$P' = \frac{1}{r_{AcAcC}} - r_{CAcC}\,Q'$$

where

$$P' = x_c\left[\left(\frac{r_{AcCC}x_c(1 + r_{CCC}x_c)}{1 + x_c r_{AcCC}} + 1\right)\Big/(N_c - 1) - 2\right]$$

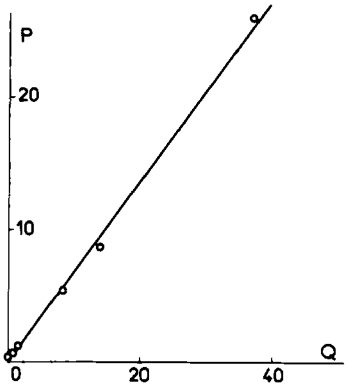


Fig. 2. Antepenultimate effect for the CC radicals in vinyl chloride (C)–vinyl acetate (Ac) copolymerization.

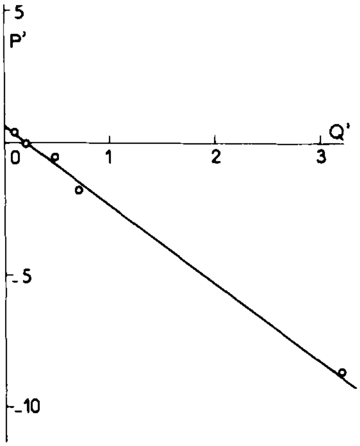


Fig. 3. Antepenultimate effect for the AcC radicals in vinyl chloride (C)–vinyl acetate (Ac) copolymerization.

$$Q' = x_c^2 \left[ \left( \frac{r_{AcCC} x_c (1 + r_{CCC} x_c)}{1 + r_{AcCC} x_c} \right) \Big/ (N_c - 1) - 1 \right]$$

and the corresponding plot, illustrated on Fig. 3, yields $r_{AcAcC} = 1.65$ and $r_{CAcC} = 3.10$. A few iterations lead to the definitive values $r_{AcCC} = 4.60$, $r_{CCC} = 1.67$ and $r_{CAcC} = 2.20$, $r_{AcAcC} = 2.0$. It may be observed that these values imply that the penultimate effect on the radicals ended by the two succession units AcC is negligible and this fact is confirmed by the absence of penultimate effect on the Ac-ended radicals.

These values have been used to calculate the copolymer composition. In Table 5, the calculated n values are compared with the experimental ones. The agreement is good for $x_C$ values up to 35 but discrepancies are always observed for the extreme part of the range.

### B. Vinylidene Chloride (V)–Vinyl Acetate (Ac) Copolymerization

In this case, for a mixture rich in vinylidene chloride, precipitation of the copolymer is observed after a few per cent conversion if DMF is used as solvent. Cyclohexanone allows a better homogeneity in a larger range but pure polyvinylidene chloride remains insoluble at 60°C in this solvent. The kinetic study is rather difficult to carry out accurately for a mixture rich in V due to the very low consumption rate of the vinyl acetate.

Figure 4 illustrates the Fineman-Ross plot of the results, together with some literature data. Our results are in very good agreement with the most recent values of Yamashita et al. [13]. A straight line fits the results in the range $0 < x_V < 0.4$ rather well and leads to $r_V = 6.6 \pm 0.3$ and $r_{Ac} = 0.07 \pm 0.02$. There is no indication of a penultimate effect on the Ac-ended radicals, but there is definitely curvature in the range rich in V. The Barb equation leads to $r_{VV} = 6.6$ and $r_{AcV} = 7.3$, but is valid only for $x_V < 10$. Antepenultimate effects are again indicated by the curvature of the plots and the same procedure as above, using P vs. Q and P′ vs. Q′ plots, finally leads to $r_{VVV} = 5.30$, $r_{AcVV} = 11.5$ and $r_{VAcV} = 6.0$, $r_{AcAcV} = 8.0$. The antepenultimate effect onto the AcV radicals is rather weak, in agreement with the fact that no penultimate effect has been observed on the Ac radicals. The calculated values of $n_V$, using the above values for the reactivity ratios, compared with the experimental ones in

Table 5. Calculated and Experimental Copolymer Compositions

| Vinyl chloride–vinyl acetate | | | Vinylidene chloride–vinyl acetate | | | Vinyl chloride–vinylidene chloride | | |
|---|---|---|---|---|---|---|---|---|
| $x_C$ | $n_C$ exptl | $n_C$ calcd | $x_V$ | $n_V$ exptl | $n_V$ calcd | $x_V$ | $n_V$ exptl | $n_V$ calcd |
| 42.9 | 64.0 | 73.9 | 43.1 | 186 | 230 | 37.2 | 113.5 | 110 |
| 33.5 | 57.0 | 57.5 | 26.9 | 119 | 144 | 17.5 | 50.7 | 51.1 |
| 14.6 | 25.8 | 25.8 | 17.4 | 94.2 | 93 | 10.6 | 25.6 | 31.7 |
| 8.95 | 16.25 | 16.27 | 14.1 | 77.2 | 76.0 | 2.9 | 8.9 | 9.1 |
| 4.50 | 7.50 | 8.70 | 9.76 | 63.5 | 53.2 | 1.81 | – | 5.83 |
| 2.15 | 4.70 | 4.61 | 3.54 | 20.9 | 20.6 | 0.57 | 2.18 | 2.05 |
| 1.05 | 2.45 | 2.54 | 0.21 | 1.85 | 1.91 | 0.111 | 0.47 | 0.47 |
| 0.45 | 1.22 | 1.24 | 0.11 | 0.98 | 1.10 | 0.053 | 0.21 | 0.23 |
| 0.15 | 0.45 | 0.46 | 0.058 | 0.66 | 0.64 | 0.020 | 0.09 | 0.09 |
| 0.03 | 0.104 | 0.106 | 0.038 | 0.39 | 0.44 | | | |
| | | | 0.014 | 0.175 | 0.179 | | | |

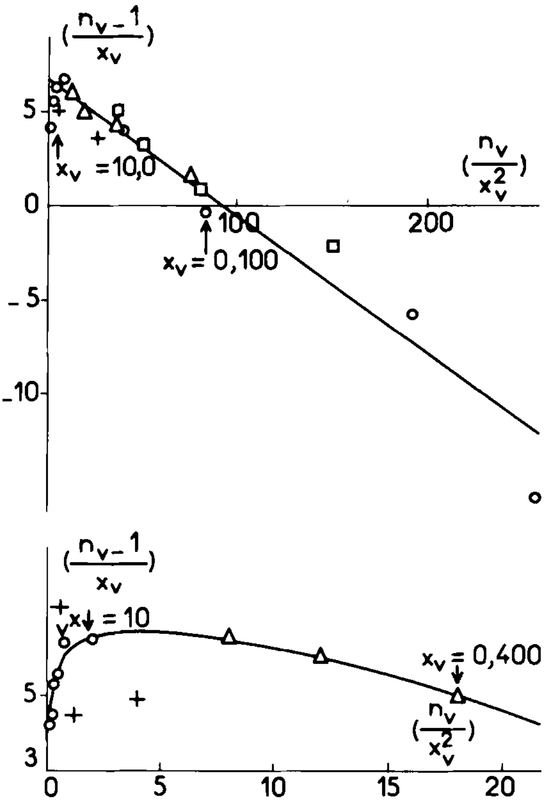


Fig. 4. Vinylidene chloride (V)–vinyl acetate (Ac) copolymerization, Fineman-Ross plot. (+) Agron et al. [6]; (△) Yamashita et al. [13]; (□) Johnsen and Kolbe [14]; and (○) this study.

Table 5, are in good agreement for $x_V \leqslant 25$ but rather large departures are observed in the extreme range.

### C. Vinyl Chloride (C)–Vinylidene Chloride (V) Copolymerization

The results of this copolymerization, carried out in THF, are shown in the Fineman-Ross plot of Fig. 5. Our results are in good agreement with the literature data, and especially with those of the recent work by Enomoto [9]. The straight line, valid for all values of $x_V < 1$, leads to $r_V = 3.25 \pm 0.16$ and $r_C = 0.22 \pm 0.02$, in agreement with most

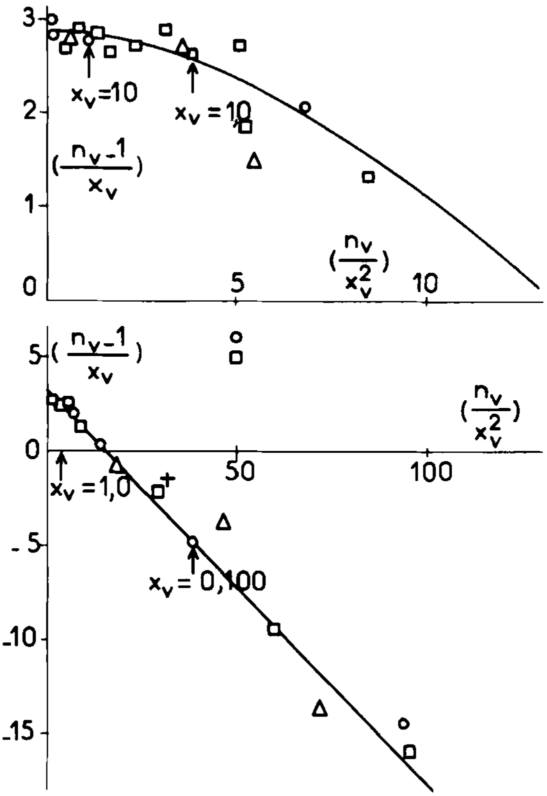
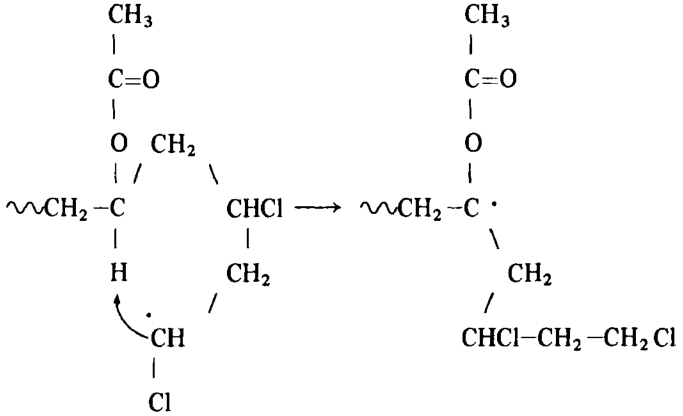


Fig. 5. Vinyl chloride (C)–vinylidene chloride (V) copolymerization, Fineman-Ross plot. (□) Enomoto [9]; (+) Agron et al. [6]; (△) Germar [12]; and (○) this study.

of the literature data (Table 1). There is no indication of a penultimate effect on the C radicals, but an important penultimate effect is observed on the V radicals. Use of the Barb equation leads to $r_{VV} = 2.94$ and $r_{CV} = 4.31$. The values of n calculated with the above values are in good agreement with the experimental ones over the entire range of monomer feed compositions (Table 5).

## III. DISCUSSION

There is a large similarity for the two systems containing vinyl acetate: no or weak penultimate effects for the Ac-ended radicals, no or weak antepenultimate effect for the AcC-ended radicals, but rather large antepenultimate effect for the CC-ended radicals. A possible explanation for the antepenultimate effect might be the occurrence of an internal transfer (back bitting) reaction.



The possibility of internal-transfer reaction has been pointed out by Melville and Sewell [22], although the preferential site of transfer was the methyl group of the acetate rather than the methine group [23]. However, it is more probable that an internal transfer on the methyl group would involve a penultimate effect rather than the observed antepenultimate effect.

The structure of the transferred radical, according to the mechanism suggested above, is close to that of a vinyl acetate radical. The difference is that a tertiary hydrogen atom is replaced by a chain of two vinyl chloride units. It is interesting to note that in both cases the values $r_{AcCC}$ or $r_{AcVV}$ are not very different from that of $1/r_{Ac}$. The values for the vinyl choride system are $r_{AcCC} = 4.60$ and $1/r_{Ac} = 3.45 \pm 0.3$, and for the vinylidene chloride system $r_{AcVV} = 11.5$ and $1/r_{Ac} = 14.5 \pm 4$.

In both cases also, the remote effect theory fails to fit exactly the results for the mixtures poor in vinyl acetate; the consumption of vinyl acetate increases more rapidly than expected when its concentration decreases. Vinyl acetate is never rigorously pure and always contains a minor amount of formaldehyde. Chromatographic analysis has shown that this amount tends to increase during the copolymerization; a possible explanation would be that formaldehyde comes from an acid-catalyzed hydrolysis of vinyl acetate. The formation of small amount of acid during the polymerization of vinyl chloride has been proved recently [24]. It is obviously hydrochloric acid produced through a radical-induced dehydrochlorination of the polymer; on the other hand, copolymers of vinyl chloride with vinyl acetate have been shown by dehydrochlorination to be less stable than homopolymers [25]. Finally, vinylidene chloride polymers are less stable than vinyl chloride polymers. Thus it may be concluded that extra consumption of vinyl acetate through hydrolysis process is quite possible.

For the vinyl chloride–vinylidene chloride system, the penultimate effect caused by a vinyl chloride unit on a vinylidene chloride radical is probably due to another kind of mechanism. Steric hindrance is probably ruled out because vinylidene chloride is the larger molecule. Up to now, we have no experimental data to support any explanation.

## REFERENCES

[1] J. Guillot, J. Vialle, and A. Guyot, *J. Macromol. Sci.–Chem.*, **A5**, 751 (1971).

[2] J. Schaefer, *J. Phys. Chem.*, **70**, 1975 (1966).

[3] C. E. Wilkes, J. C. Westfahl, and R. H. Backderf, *J. Polym. Sci., Part A1*, **7**, 23 (1969).

[4] F. R. Mayo, C. Walling, F. M. Lewis, and W. F. Hulse, *J. Amer. Chem. Soc.*, **70**, 1523 (1948).

[5] N. Grassie, I. C. McNeill, and I. F. McLaren, *J. Polym. Sci., Part B*, **3**, 897 (1965).

[6] P. Agron, T. Alfrey, T. Bohrer, H. Haas, and H. Wechsler, *J. Polym. Sci.*, **3**, 157 (1948).

[7] K. Hayashi and T. Otsu, *Makromol. Chem.*, **127**, 54 (1969).

[8] C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Shertz, *J. Amer. Chem. Soc.*, **64**, 2356 (1942).

[9] S. Enomoto, *J. Polym. Sci.*, **55**, 95 (1961).

[10] F. R. Mayo, F. M. Lewis, and C. Walling, *J. Amer. Chem. Soc.*, **70**, 1529 (1948).

[11] G. V. Tkachenko, P. H. Khomikovski, A. D. Abkin, and S. S. Medvedev, *Zh. Fiz. Khim.*, **31**, 242 (1957).

[12] V. H. Germar, *Makromol. Chem.*, **84**, 36 (1965).
[13] Y. Yamashita, K. Ito, H. Ishii, S. Hoshino, and M. Kai, *Macromolecules*, **6**, 1 (1968).
[14] V. U. Johnsen and U. K. Kolbe, *Kolloid Zh.*, **216**, 97 (1966).
[15] K. Ito, S. Iwase, and Y. Yamashita, *Makromol. Chem.*, **110**, 233 (1967).
[16] K. Doak, *J. Amer. Chem. Soc.*, **70**, 1525 (1948).
[17] Y. Yamashita, K. Ito, S. Ikuwa, and H. Kada, *J. Polym. Sci., Part B*, **6**, 219 (1968).
[18] A. Guyot and J. Guillot, *J. Chim. Phys.*, **61**, 1434 (1964).
[19] M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
[20] W. G. Barb, *J. Polym. Sci.*, **11**, 117 (1953).
[21] G. E. Ham, *J. Polym. Sci.*, **14**, 87 (1954).
[22] H. W. Melville and P. R. Sewell, *Makromol. Chem.*, **32**, 139 (1959).
[23] S. Imoto, J. Ukida, and T. Kominami, *Kobunshi Kagaku*, **14**, 101 (1957).
[24] S. Enomoto, *J. Polym. Sci., Part A1*, **7**, 1255 (1969).
[25] N. Grassie, I. F. McLaren, and I. C. McNeill, *Eur. Polym. J.*, **6**, 679 (1970).

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