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Vinyl Chloride-Vinylidene Chloride Copolymerization: Kinetic Deviations and Structural Defects

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ABSTRACT

The penultimate effect in the radical copolymerization of vinyl chloride (C) and vinylidene chloride (V), described in a previous paper, is interpreted in terms of head-to-head addition of a V molecule to a C-ended radical. The later is estimated from NMR analysis of the copolymer. It occurs about three times faster than the corresponding head-to-tail addition. It is shown that both the penultimate effect model and the "head-to-head assumption" lead to the same values for either the copolymer composition or several functions of the sequence distribution. It is further suggested that the head-to-head addition is possible owing to the propagation-depropagation equilibrium for the V-ended radical and to the very high reactivity of the tail radical produced.

INTRODUCTION

In a previous paper [1] it was shown that a penultimate effect on the vinylidene chloride-ended radical might explain the kinetics results of vinyl chloride (C)-vinylidene chloride (V) radical copolymerization. The following reactivity ratios (R) have been derived.

$$R_C = 0.22 \qquad R_{VV} = 2.94 \qquad R_{CV} = 4.31$$

However, no explanation has been proposed for this effect. On the other hand, some features of the NMR spectra of CV copolymers have been interpreted by Chujo et al. [2] and also McClanahan and Previtera [3] in terms of a head-to-head addition of a V unit to a C-ended radical, followed by a tail-to-tail addition between two V units to give a sequence of two methylene groups. Later, Johnsen [4] and Enomoto and Satoh [5] proposed another interpretation based on consideration of the distribution of the tetrads CCCC, VCCC, VCCV, CCVC, CCVV, VCVC, VCVV, CVVC, VVVC, and VVVV. Yamashita et al. [6] have shown that the last interpretation was consistent with the sequence distribution calculated from the classical copolymerization theory using reactivity ratios $r_V = 4.15$ and $r_C = 0.16$. However, these reactivity ratios are rather different from ours and do not take into account the deviations from theoretical kinetics observed by Enomoto [7] and in our previous study [1] in the vinylidene chloride-rich region of the monomer feed range.

The purpose of the present paper is to show that the head-to-head addition actually occurs and may give an account for the kinetic results.

EXPERIMENTAL

The copolymers were prepared using radical polymerization at 60°C in tetrahydrofuran solution. Their composition and structural properties are reported in Table 1. The rather low molecular weight obtained is undoubtedly due to the fact that tetrahydrofuran is a powerful transfer agent. The NMR spectra have been taken from hexachloroacetone solutions at 140°C using a Varian DA 60 IL spectrometer and a JEOL-JRA-1 spectrum accumulator.

TABLE 1. Data for the Copolymers Studied

Copolymer Reference	Composition (mole %)		Kinetic data		Conversion (%)					
No.	C	V	x_C	n_C	C	V	$\overline{M}_n$	α_H (%)	α_C (%)	VCV (%)
I	72	28	19	2.57	3	10	1200	3.7	96.3	3.0
II	61	39	8.6	1.56	0.5	1.5	-	5.3	94.7	11.0
III	43	57	3.6	0.76	1	3	-	8.25	91.75	31.0
IV	21	79	1.66	0.26	3	8	1500	16.50	83.50	52.0
V	16	84	0.34	0.12	1.5	3.6	1500	33.50	66.50	86.0
VI	7	93	0.095	0.039	0.8	2.4	-	72.50	27.50	98.0

RESULTS AND DISCUSSION

NMR Spectra

A characteristic feature of the head-to-head addition is the occurrence of an α-proton (α_H) of a vinyl chloride unit in the sequence $-CH_2-CHCl-CCl_2-$ (I). Structure I may also arise from a coupling cross-termination reaction: however, such an event is not frequent because the kinetic chain is rather long at the polymerization temperature used. Structure I has been observed in the NMR spectrum of chlorinated polyethylene [8]; the corresponding α-proton resonance is located at 4.1 τ. In the present case its detection requires spectra accumulation because Structure I becomes important only for the vinylidene chloride-rich copolymers and in this range the total number of α-protons is low. Figure 1 shows a typical accumulated spectrum of the α-protons. From the area under the α_H-triplet at 4.1 τ and the α_C-quintuplet centered at 5.4 τ, which corresponds to the normal α-protons of polyvinyl chloride, one obtains the mole % of C units engaged in a head-to-head structure. The results reported in Table 2 show that the richer in V is the monomer feed, the more important is the head-to-head propagation mode. This fact suggests a possible correlation, studied in more detail below between the amount of α_H-protons and the length of the C sequences.

The spectra of β-protons are much more complex. As is well known, there is only one single narrow line at 6.2 τ for the polyvinylidene chloride, and a multiplet between 7.5 and 8.3 τ for the polyvinyl chloride homopolymers. The spectra of the copolymers (Fig. 2) exhibit some features described by Johnsen [4] and Satoh and Enomoto [5]. Their resolution is not good owing to a degradation reaction during the measurement at 130°C. A C-rich copolymer has three main resonance groups in the regions 6.2-6.6, 6.9-7.4, and 7.5-8.3. A V-rich copolymer shows a spectrum identical to that published by Previtera [3]: a narrow and intense singlet at 6.2 τ and a small group of peaks at 6.4 τ. The last one has been assigned to the tail-to-tail methylene groups which come from the following set of reactions:

$$\sim\sim CH_2-\dot{C}HCl + CCl_2{=}CH_2 \longrightarrow \sim\sim CH_2-CHCl-CCl_2-\dot{C}H_2$$

head-to-head addition (1)

$$\sim\!\sim CH_2-CHCl-CCl_2-\dot{C}H_2 + CH_2{=}CCl_2 \longrightarrow \sim\!\sim CH_2-CHCl-CCl_2-CH_2-CH_2-\dot{C}Cl_2 \quad \text{tail-to-tail addition} \tag{2}$$

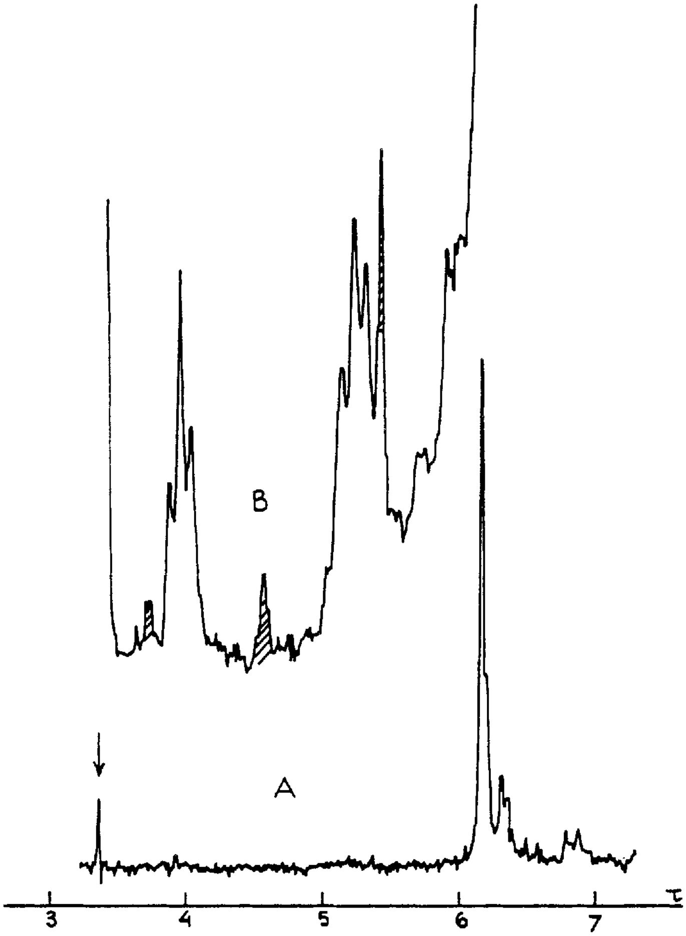

FIG. 1. NMR spectra of (vinyl chloride-vinylidiene chloride) copolymer with 90% vinylidene chloride. Solvent, hexachloroacetone. T°C = 130. A: Single scan spectrum. B: Accumulated spectrum (256 scans). The arrow and the cross-hatched spectra indicate solvent impurities).

TABLE 2. Comparison between Experimental and Calculated Compositions of Copolymers

x_V	37.2	17.5	10.6	2.9	0.57	0.111	0.053	0.020
n_V, expt	109.0	51.0	32.5	9.00	2.18	0.47	0.21	0.090
n_V, calc [1]	110.0	51.1	31.7	9.1	2.05	0.47	0.23	0.090
n_V, calc (this work)	110.3	52.1	31.7	9.00	2.04	0.465	0.228	0.089

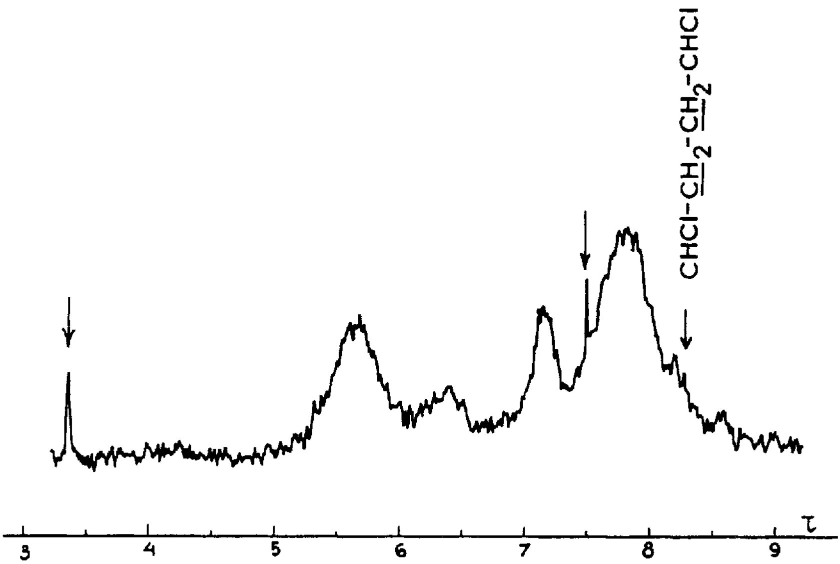

FIG. 2. NMR spectrum of (vinyl chloride-vinylidene chloride) copolymer with 47% vinylidene chloride. The arrows indicate solvent impurities.

It has been assumed that, by analogy with the case of polyvinylidene fluoride [9], a tail-to-tail addition occurs quasi-exclusively after a head-to-head addition. The same conclusion may be drawn from theoretical calculations based on molecular orbital theory [10]. On the other hand, after Johnsen [4], the same absorption of 6.4 τ is assigned to the central methylene groups of a regular CVVV tetrad. There is no data in the literature about the spectra of model compound such as $CH_3-CCl_2-CH_2-CH_2-CCl_2-CH_3$, but the chemical shift of that structure, compared to the one of $-CCl_2-CH_2-CCl_2-$, may be estimated to be less than 0.5 τ upfield, by comparison with oxygenated compounds and taking in account the fact that either an oxygen atom in the chain or a carboxylic group contributes a magnetic anisotropy larger than do the chlorine atoms. The resonance of the CH_2 groups in dimethoxymethane and dimethoxyethane takes place at 4.5 and 3.34 τ, respectively ($\Delta\tau$ = 1.12 τ), while for the same group in ethyl malonate or succinic ester the values are 3.37 and 2.62 τ, respectively ($\Delta\tau$ = 0.7 τ).

This results in the absorption of the structure characteristic of the head-to-head addition being indistinguishable from that of the CVVV or CVVC tetrads. The head-to-head addition may also involve a vinylidene chloride radical unit and a vinyl chloride monomer, leading to the tail-to-tail structure $-CHCl-CH_2-CH_2-CCl_2-$ (II) or $-CHCl-CH_2-CH_2-CHCl-$ (III), depending on which monomer adds to the methylene-ended radical. The model compound of Structure III (1-4 dichlorobutane) has its resonance line at 8.2 τ [12] which, compared to the $-CHCl-CH_2-CHCl-$ spectrum, corresponds to a chemical shift of about 0.3 τ only. Beyond the resonance of the protons of $-CHCl-CH_2-CHCl-$ in a C-rich copolymer (Fig. 2), the presence of a shoulder at the high field side of the spectrum suggests that the tail-to-tail addition (III) might actually occur, but only with a small probability.

Kinetic Study

At a first approximation, it seems possible to neglect the head-to-head addition of a C monomer to a V-ended radical. Taking into account only the head-to-head addition of a V monomer to a C-ended radical together with the four (normal) head-to-tail additions, and assuming further that a head-to-head addition is followed exclusively by a tail-to-tail addition, we have to consider three different radicals: regular C or V head-ended radicals $\sim\!\sim CH_2-\dot{C}HCl$ ($C^{\cdot}$) and $\sim\!\sim CH_2-\dot{C}Cl_2$ ($V^{\cdot}$), and a tail radical $\sim\!\sim CCl_2-\dot{C}H_2$ ($T^{\cdot}$). Propagation reactions are as follows:

$$C^{\cdot} + C \xrightarrow{K_{CC}} C^{\cdot} \tag{3}$$

$$C^{\cdot} + V \xrightarrow{K_{CV}} V^{\cdot} \quad \text{regular addition} \tag{4}$$

$$C^{\cdot} + V \xrightarrow{K_{CT}} T^{\cdot} \quad \text{head-to-head addition} \tag{1}$$

$$V^{\cdot} + C \xrightarrow{K_{VC}} C^{\cdot} \tag{5}$$

$$V^{\cdot} + V \xrightarrow{K_{VV}} V^{\cdot} \tag{6}$$

$$T^{\cdot} + C \xrightarrow{K_{TC}} C^{\cdot} \tag{7}$$

tail-to-tail addition

$$T^{\cdot} + V \xrightarrow{K_{TV}} V^{\cdot} \tag{8}$$

The corresponding reactivity ratios are defined

$$r_C = K_{CC}/K_{CV} \qquad r_{CT} = K_{CC}/K_{CT} \qquad r_V = K_{VV}/K_{VC}$$

$$r_T = K_{TV}/K_{TC}$$

Using the steady-state assumption, and calculating - dC/dt and - dV/dt,

$$n = \frac{dV}{dC} = \frac{\frac{1}{r_C} + \frac{1}{r_{CT}} + \frac{r_V}{r_C}x + \frac{r_T}{r_{CT}}x\frac{1 + r_V x}{1 + r_T x}}{\frac{1}{r_C} + \frac{1}{r_{CT}} + \frac{1}{x}} \tag{9}$$

where x = V/C is the ratio of monomer concentrations. It is not possible to derive the value of the four reactivity ratios from this equation. However, it is possible to get the values of r_V and of the expression $(1/r_C) + (1/r_{CT})$ from the extrapolated values of plots of n/x when x tends to be infinite or null, respectively.

A simplifying assumption is to consider the case where the head-to-head addition of the C-ended radical to the V monomer is exclusive. Then $K_{CV} = 0$, $1/r_C = 0$. Equation (9) becomes

$$n = \frac{1 + r_T x\frac{1 + r_V x}{1 + r_T x}}{1 + (r_{CT}/x)} \tag{9'}$$

It is recognized that this equation does correspond exactly to that of the penultimate effect limited to the V radical. Then we have

$$r_{CT} = R_{CC} = 0.22 \qquad r_T = R_{CV} = 4.31 \qquad \text{and}$$

$$r_V = R_{VV} = 2.94.$$

The fact that such an equation gives a good fit of the experimental data in the whole range of composition [1] might incline us to consider that exclusive head-to-head addition followed by exclusive tail-to-tail addition is the actual cause of the kinetic anomaly. However, as shown later, the exclusive addition has to be ruled out except, perhaps, in the limiting condition of V-rich copolymerization.

The possible occurrence of a head-to-head addition of a C monomer to a V-ended radical might lead us to consider a more complex scheme including two tail radicals and ten propagation reactions. This scheme leads to a very complex kinetic equation which is not tractable by itself. Extrapolation procedures are possible again, but the only way to determine the various reactivity ratios would be to measure the methylene absorptions of the tail-to-tail addition by the NMR spectra. This is not possible, but the simple consideration of only one kind of head-to-head addition is sufficient to give a good account of the experimental results.

Derivation of the Reactivity Ratios

Figure 3 shows a plot of n/x vs x in the range of low values of x. From that plot one obtains from Eq. (9)

$$\frac{1}{r_C} + \frac{1}{r_{CT}} = 4.5 \pm 0.2 \qquad (10)$$

On the other hand, Fig. 4 shows the plot of n/x vs 1/x for high values of x from which one obtains

$$r_V = 3.0 \pm 0.1$$

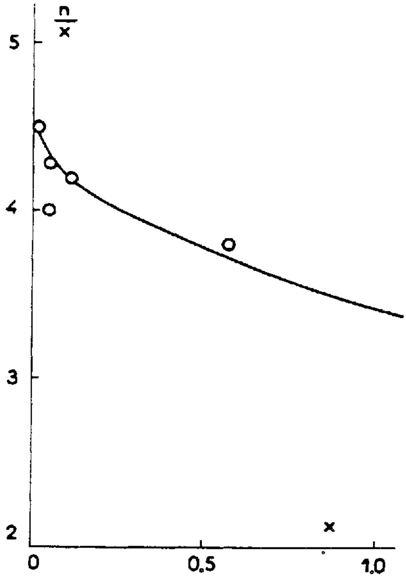

FIG. 3. Kinetics results for monomer feed rich in vinyl chloride.

In order to obtain r_C and r_{CT} it is necessary to derive the amount of α_H-protons in the copolymer. It is possible to calculate, from kinetics, the ratio $d\alpha_H/dC$ of the α_H-protons over the total number of α-protons of C units engaged in the copolymer under given conditions. On the other hand, the NMR data give the proportion of α_H-protons in the whole copolymer.

The total number of α_H-protons is given by

$$\alpha_H = p(C_o - C)$$

where C_o and C are concentrations of C units at the beginning of the process and at the time of sampling, respectively. Then

$$\frac{d\alpha_H}{dt} = \frac{d}{dt}[p(C_o - C)] = \frac{dp}{dt}(C_o - C) - p\frac{dC}{dt}$$

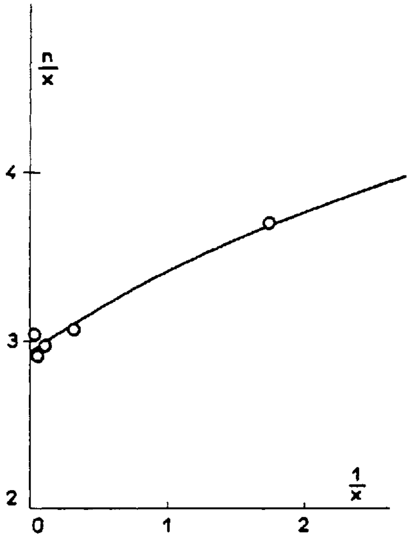

FIG. 4. Kinetics results for monomer feed rich in vinylidene chloride.

This results in

$$\frac{d\alpha_H}{dC} = -p + (C_o - C)\frac{dp}{dC} \tag{11}$$

Now, kinetically, $d\alpha_H/dt = k_{CT}C^{\cdot}V$ and

$$\frac{dC}{dt} = -[K_{CC}C^{\cdot}C + k_{VC}V^{\cdot}C + k_{TC}T^{\cdot}C]$$

Using the steady-state assumption, one obtains

$$-\frac{d\alpha_H}{dC} = \frac{1}{(r_C/x) + (r_{CT}/r_C) + 1} \tag{12}$$

which may be simplified, if one assumes an exclusive head-to-head addition, to

$$-\frac{d\alpha_H}{dC} = \frac{1}{1 + (r_{CT}/x)} \tag{12'}$$

From (11) and (12) one obtains

$$\frac{1}{1 + \frac{r_C}{x} + \frac{r_{CT}}{r_C}} = p - (C_o - C)\frac{dp}{dC} \tag{13}$$

Practically, it is not possible to integrate Eq. (13). When the conversion is rather large, it is necessary to derive dp/dC in order to integrate Eq. (13). From the definition of x, one has x = V/C. Then

$$dV = xdC + Cdx \qquad \text{or} \qquad n = dV/dC = x + C(dx/dC)$$

On the other hand, one has

$$C_o\left(1 - \frac{C}{C_o}\right)\frac{dp}{dC} = \frac{dp}{dC}\, C_o \rho$$

where ρ is the yield:

$$C_o\left(1 - \frac{C}{C_o}\right)\frac{dp}{dC} = \frac{dp}{dx}\,\frac{\rho}{1 - \rho}\,(n - x)$$

Finally

$$-\frac{d\alpha_H}{dC} = \frac{1}{1 + \frac{r_C}{x} + \frac{r_{CT}}{r_C}} = p - \frac{dp}{dx}\,\frac{\rho}{1 - \rho}\,(n - x) \tag{13'}$$

Given the expression of n (Eq. 9), all the terms of Eq. (13') may be obtained from experimental results or their graphical expression (plot of p vs x). However, Eq. (13') is rather complex and it is better to use data from low conversion experiments. In such a case, the second term of the left-hand side of Eq. (13) may be neglected and one has, more simply,

$$1/p = 1 + (r_{CT}/r_C) + (r_C/x) \tag{13''}$$

It results that if $1/x \rightarrow 0$, $1/p \rightarrow 1 + (r_{CT}/r_C)$

From a plot of Eq. (13") (Fig. 5) one obtains

$$1 + (r_{CT}/r_C) = 1.3 \pm 0.2 \tag{14}$$

For an exclusive head-to-head addition, the plot of Fig. 5 would have to be extrapolated to 1 instead of to 1.3. On the other hand, the plot is not a straight line, as expected from Eq. (13'). Deviation occurs for C-rich copolymers. In this range of composition, the second kind of head-to-head addition (C monomer to a V-ended radical) might not be negligible so that p might be overestimated and 1/p lowered in the plot. Unfortunately, it does not seem possible to make the correction quantitatively.

Combining Eqs. (10) and (14) yields $r_C = 1.0 \pm 0.3$ and $r_{CT} = 0.30 \pm 0.03$.

The fourth reactivity ratio, r_T, cannot be derived directly, but using Eq. (9) and a trial and error process in a computer, one obtains $r_T = 4.5 \pm 0.5$.

Using $r_C = 1.0$, $r_{CT} = 0.30$, $r_V = 3.0$ and $r_T = 4.5$ and Eq. (9), one obtains the calculated values of the last line of Table 2, which are in good agreement with the experimental values.

Relations with Sequence Distributions

The increasing proportion of α_H-protons with decreasing vinyl chloride concentration suggests that the head-to-head addition might be specific for isolated C units. On the basis of the preceding

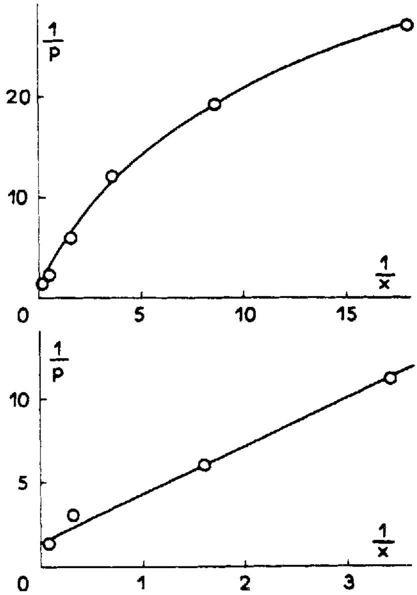

FIG. 5. Inverse plot of the proportion of α-protons (α_H) of vinyl chloride units engaged in head-to-head addition vs the monomer feed ratio.

scheme, we have calculated the amount of isolated C units.

The treatment was based on the methods proposed by Ito and Yamashita [11]. The probability of the existence of isolated C units is the sum of probabilities of the four following triads: TCV, VCV, VCT, and TCT, where T represents a V unit added in a head-to-head position (giving a tail radical). Following Ito and Yamashita, one obtains

$$[TCV] = [TC]p_{tcv} = [T]p_{tc}p_{tcv} = [V]p_{tc}p_{cv} \qquad (15)$$

$$[VCV] = [VC]p_{vcv} = [V]p_{vc}p_{vcv} = [V]p_{vc}p_{cv} \qquad (16)$$

$$[VCT] = [VC]p_{vct} = [V]p_{vc}p_{vct} = [V]p_{vc}p_{ct} \qquad (17)$$

$$[TCT] = [TC]p_{tct} = [T]p_{tc}p_{tct} = [V]p_{tc}p_{ct} \tag{18}$$

The terms in brackets represent the probability of existence of the corresponding triad, diad, or unit, and the p_{xyz} represent the conditional probabilities of addition of a z unit to a xy-ended radical. The last terms in Eqs. (15) to (18) imply that [T] is a part of [V] and that there are no penultimate effects. Then

$$[\text{isolated C}] = [V]\,(p_{cv} + p_{ct})\,(p_{tc} + p_{vc}) \tag{19}$$

Now, from the usual definitions,

$$n = [V]/[C] = p_{cv}'/p_{vc}'$$

where p' is the total conditional probabilities of addition of a unit on an x-ended radical, and where the kind of addition (head-to-head or head-to-tail) is not differentiated.

One also has

$$p_{cv}' = \frac{k_{cv}C^{\cdot}V + k_{ct}C^{\cdot}V}{k_{cv}C^{\cdot}V + k_{ct}C^{\cdot}V + k_{cc}C^{\cdot}C} = p_{cv} + p_{ct}$$

Similarly

$$p_{vc}' = p_{vc} + p_{tc}$$

Finally

$$[\text{isolated C}] = [C](p_{cv} + p_{ct})^2 \tag{20}$$

so that the proportion of isolated C units among the C units is

$$\% \text{ isolated C} = \left[\frac{1}{1 + \dfrac{1}{x\left(\dfrac{1}{r_C} + \dfrac{1}{r_{CT}}\right)}}\right]^2 \qquad (21)$$

Figure 6 shows a plot of the proportion of isolated units vs 1/x together with a plot of the proportion of α_H-protons. It seems that the two plots are definitely different. It is obvious that other functions of the sequence distribution cannot exist such as the proportion of diads, etc. which might correlate with the proportion of α_H-protons. Thus it may be concluded that the head-to-head addition cannot be correlated with the sequence distribution and that it cannot be accounted for in terms of remote unit effects. In conclusion, the kinetic deviations from the classical Lewis-Mayo theory of radical copolymerization observed in the case of vinyl chloride-vinylidene chloride copolymerization may be explained on the basis of a head-to-head addition of a vinylidene unit to a

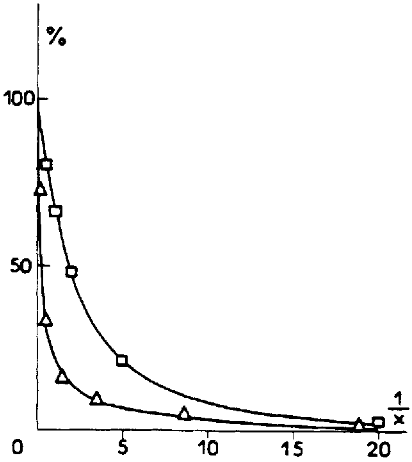

FIG. 6. Proportion of isolated vinyl chloride units (□) compared with α_H protons (△) vs the monomer feed ratio.

vinyl-ended radical which occurs with a rate constant about three times higher than the corresponding head-to-tail addition.

Comparison with the Penultimate Effect Model

The data given in Table 2 show that the head-to-head assumption and the penultimate model [1] are both in good agreement with the experimental results for n. It may be shown further that Eq. (9) may be rewritten in a form close to that of the penultimate model. One has

$$n = \frac{\left[\frac{1}{r_C} + \frac{1}{r_{CT}}\right] + \left[\frac{r_V}{r_C} + \frac{r_T}{r_{CT}}\frac{1 + r_V x}{1 + r_T x}\right]x}{\left[\frac{1}{r_C} + \frac{1}{r_{CT}}\right] + \frac{1}{x}} =$$

$$\frac{1 + \dfrac{\left[\frac{r_T}{r_{CT}} + \frac{r_V}{r_C}\frac{1 + r_T x}{1 + r_V x}\right] \times \left[\frac{1 + r_V x}{1 + r_T x}\right]}{\frac{1}{r_C} + \frac{1}{r_{CT}}}}{1 + \left(\frac{r_C r_{CT}}{r_C + r_{CT}}\right)\frac{1}{x}} \qquad (9')$$

Using the values obtained above, it is easy to show that in the range $0 < x < \infty$, the first term in brackets on the right-hand side of Eq. (9'), namely

$$A = \frac{r_T}{r_{CT}} + \frac{r_V}{r_C}\frac{1 + r_T x}{1 + r_V x}$$

yields values in the range $4.2 < A < 4.5$, which correspond to the value chosen for r_T. The penultimate equation actually involves $R_{CV} = A = r_T = 4.3$, $R_{VV} = r_V \simeq 3$, and $R_C = 0.22 = r_C r_{CT}/(r_{CT} + r_C)$.

Actually, as shown in Fig. 7, it is not surprising that the various functions of the sequence distribution, such as the run number of Harwood [13], or the average length of the V or C sequences, leads to the same values for the two models assumed.

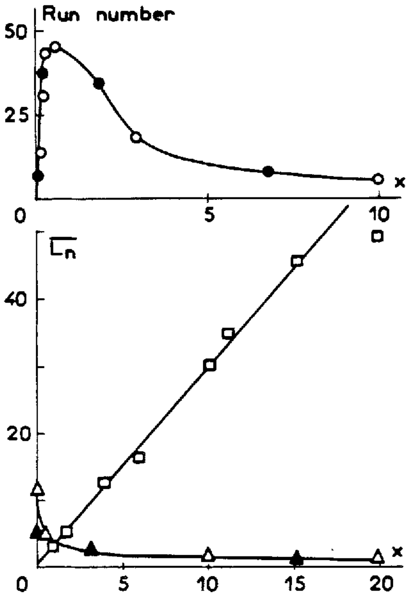

FIG. 7. Run number of Harwood [13] (○), average length of vinylidene chloride (□), or of vinyl chloride (△) sequences for the penultimate model (○ , □ , △) and for the "head-to-head assumption" (● , ■ , ▲).

DISCUSSION

Based to the assumption of the occurrence of the head-to-head addition of a V unit to a C-ended radical, the result obtained might be explained as follows: The propagation constant for vinylidene chloride homopolymerization (8.6 at 25°) is very low compared to vinyl chloride homopolymerization (6200 at 25°C) [14]. The reason is probably due to a propagation-depropagation competition during and after the transition state. The addition mode is definitely fixed only when the radical product has reacted with another monomer molecule. Such a situation is probably also true for any addition reaction of any monomer unit to any radical. Then the probability of an addition step depends not only on the corresponding propagation rate, but also on the reactivity of the radical product. Theoretical studies [10] point out the very high reactivity of the tail radicals and the high value of ΔE_{rs}, π-conjugation energy, for the tail-to-tail addition compared with the regular head-to-tail addition. Then, although the head-to-head addition of a V unit on a C-ended radical would undoubtedly be less probable than the corresponding head-to-tail addition, the resulting radical might be very much more reactive, leading to a final probability of the sequences of reactions (1)-(7) plus (1)-(2) being three times larger than that of the sequence (4)-(5) plus (4)-(6). Further, the depropagation reaction for V-V• structure is certainly easier than the corresponding reaction for the V-C• structure, so that the head-to-head addition becomes more frequent when the V content is higher. On this basis also, it is possible to understand why the head-to-head addition is much more pronounced for the C-V addition than for the V-C addition.

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