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Dichlorobutyl Branch Formation and the Question of Diffusion-Controlled Propagation in the Polymerization of Vinyl Chloride

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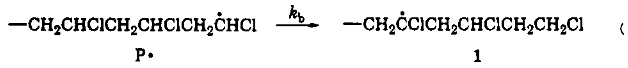
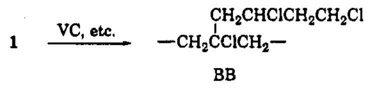
ABSTRACT: Previously published concentrations ($\bar{\varrho}_{BB}$'s) of the 2,4-dichloro-*n*-butyl branches in poly(vinyl chloride) (PVC) have been used to develop a simple theory that predicts $\bar{\varrho}_{BB}$ values as a function of monomer concentration and temperature during polymerization. The experimental values of $\bar{\varrho}_{BB}$ are shown to be consistent, quantitatively, with the well-known "back-biting" mechanism for dichlorobutyl branch formation. They also indicate that the activation energy for back-biting is greater than that for normal chain propagation by 4.4 kcal/mol. In monomer-swollen PVC at 45–80 °C, back-biting:propagation rate-constant ratios (k_b/k_p's) are invariant with monomer conversion up to total conversions of 83–91%, at least, and at 40 °C the value of k_b/k_p does not change significantly when the polymerization is carried out in 1,2-dichloroethane solution instead of in monomer-swollen polymer. These results are shown to provide strong evidence against diffusion control of the rate of chain propagation.

Structures containing tertiary chloride seem to contribute considerably to the thermal instability of poly(vinyl chloride) (PVC).[1,2] Of these, the one that occurs most frequently contains a 2,4-dichloro-*n*-butyl branch and will be designated here as BB. The detailed microstructure of this segment, established in 1981,[3] shows that it is formed during polymerization by a process involving "back-biting" by the ordinary macroradical, P• (eq 1). Subsequent addition of vinyl chloride (VC) to radical **1** in the usual head-to-tail fashion (eq 2) then produces the branch arrangement.



$$\underset{\mathrm{P}\bullet}{-CH_2CHClCH_2CHClCH_2\dot{C}HCl} \xrightarrow{k_b} \underset{\mathbf{1}}{-CH_2\dot{C}ClCH_2CHClCH_2CH_2Cl} \quad (1)$$



$$\mathbf{1} \xrightarrow{\text{VC, etc.}} \underset{\text{BB}}{-CH_2\overset{\displaystyle CH_2CHClCH_2CH_2Cl}{\overset{|}{C}}ClCH_2-} \quad (2)$$

The BB concentration per monomer unit ($\bar{\varrho}_{BB}$) can be deduced from the ^{13}C NMR spectrum of reductively dechlorinated PVC.[1-3] However, this procedure is rather time-consuming. Thus it has been desirable to develop a method for predicting $\bar{\varrho}_{BB}$ from known values of synthesis variables such as temperature of polymerization and monomer concentration. Here we describe an approach to this problem that stems directly from the following considerations. Reaction 1 must be essentially irreversible, because it is exothermic[4] and is followed by a reaction (eq 2) that is both irreversible and very fast under normal reaction conditions. Hence the rate of BB formation is described by eq 3, where

$$d[BB]/dt = k_b[P^\bullet] \qquad (3)$$

$$d[PVC]/dt = k_p[P^\bullet][VC] \qquad (4)$$

$$\bar{\varrho}_{BB} = \frac{d[BB]/dt}{d[PVC]/dt} = \frac{k_b}{k_p[VC]} \qquad (5)$$

the brackets denote concentrations. Since head-to-tail propagation is the usual fate of P•, eq 4 is an excellent approximation to the rate of VC enchainment (here, k_p is the propagation rate constant, and [PVC] represents the concentration of polymerized monomer units). Division of eq 3 by eq 4 yields a simple expression for $\bar{\varrho}_{BB}$ (eq 5) from which k_b/k_p can be obtained for a given temperature as the slope of a plot of $\bar{\varrho}_{BB}$ vs $[VC]^{-1}$.

The Arrhenius expression for k_b/k_p is eq 6. When it is combined with eq 5 in order to eliminate k_b/k_p, a relationship (eq 7) ensues that can be used to predict

$$k_b/k_p = (A_b/A_p)e^{-(E_b-E_p)/RT} \qquad (6)$$

$$\bar{\varrho}_{BB} = \frac{(A_b/A_p)}{[VC]}e^{-(E_b-E_p)/RT} \qquad (7)$$

$$-\ln(k_b/k_p) = \frac{E_b - E_p}{RT} - \ln(A_b/A_p) \qquad (8)$$

the value of $\bar{\varrho}_{BB}$ at any temperature if the values of $(E_b - E_p)$ and A_b/A_p are known. The latter values can be extracted from the slope and intercept, respectively, of plots of eq 8, which is a logarithmic version of eq 6.

Another objective of this study has been to use experimental values of $\bar{\varrho}_{BB}$ in order to test for diffusion-controlled propagation in the polymerization of VC.

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Diffusion control of propagation has been suggested to be operative in situations where liquid VC is absent, and all of the polymerization occurs, therefore, in the monomer-swollen polymer.[5] These circumstances are encountered, for example, in bulk or suspension polymerizations that are allowed to continue after the monomer phase disappears. In such situations the polymer phase will experience increases in viscosity and decreases in free volume with increasing VC conversion, because a saturation concentration of VC in the polymer is no longer being maintained. As a result of these property changes, the value of k_p in the monomer-swollen resin has been suggested to become controlled by diffusion at the point where liquid VC vanishes and to decrease continuously and quite rapidly as conversion proceeds to higher levels.[5a-d] When the total conversion is 80% at a temperature of 50 °C, for example, k_p in the polymer phase has been proposed to be less by about a factor of 10 than its value in the polymer phase when liquid monomer is still present.[5b,d] In contrast, the effect of conversion on k_b should be very minor or nonexistent if the temperature of the polymer phase remains above T_g. As long as T_g is exceeded, the growing end of $P^\bullet$ will remain torsionally mobile,[6] and its segmental diffusion actually should be facilitated by increasing conversion, owing to an increasing tendency of this end to separate from the polymer coil.[7] These factors certainly should tend to inhibit diffusion control of reaction 1. Furthermore, even if this reaction were subject to retardation by slow diffusion, much higher conversions would be needed to reach that condition than would be the case for normal chain propagation, because the former reaction is much slower than the latter process. Therefore, if normal propagation were indeed under diffusion control, the k_b/k_p ratio should rise with increasing conversion after liquid VC disappears, a conclusion that also has been reached by other workers[5a] on the basis of some of the arguments that have just been given here. As a result of the k_b/k_p increase, diffusion control of propagation should be revealed by the occurrence of upward curvature in plots of eq 5. It also should cause k_b/k_p to be higher in monomer-swollen PVC than it is in dilute solutions having relatively low viscosities. Experimental tests of these predictions are described in the present paper.

Results and Discussion

Correlation of $\bar{\varrho}_{BB}$ Values. Hjertberg and Sörvik had reported[8] a set of $\bar{\varrho}_{BB}$ values that were pleasingly self-consistent and seemed to be especially appropriate for use as data standards. These values were obtained for polymers prepared in aqueous suspensions at constant VC pressures that were defined by values of P/P_0, where P was the actual monomer pressure and P_0 was the monomer pressure that would have produced a saturation concentration of VC in the polymer at the temperature being used.[8] The P/P_0 values were less than 1 in every case.[8] Thus these were "subsaturation" polymerizations occurring in the absence of liquid monomer. They were carried out at temperatures that encompassed most of the range used commercially and with precautions designed to ensure that the concentrations of monomer in the polymer phase were not being reduced by low rates of monomer transfer into that phase from the surrounding medium.[8] In order to determine the branch concentrations, the authors[8] used a standard procedure that involves reductive dechlorination of the polymer with tri-*n*-butyltin hydride and ^{13}C NMR analysis of the "polyethylene" thus produced.[3,4,9] The reduction converts most of the dichlorobutyl branch segments into the Bu structure, but lesser amounts of the ClBu moiety usually are formed as well.[10] In the work of Hjertberg and Sörvik,[8] $\bar{\varrho}_{BB}$ values were determined correctly as sums of the concentrations of the Bu and ClBu groups.

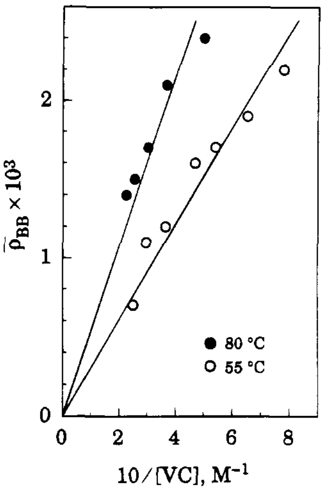


Figure 1. Plots of eq 5 made with data from ref 8 (R^2, °C): 0.96, 80; 0.96, 55.

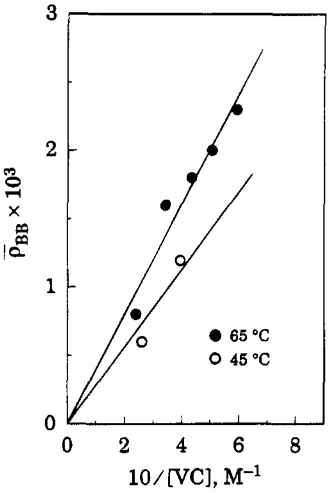
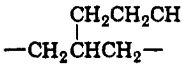
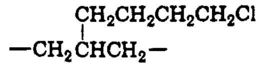


Figure 2. Plots of eq 5 made with data from ref 8 (R^2, °C): 0.98, 65; 0.97, 45.


$$-CH_2\overset{\overset{\displaystyle CH_2CH_2CH_2CH_3}{|}}{C}HCH_2-$$

Bu


$$-CH_2\overset{\overset{\displaystyle CH_2CH_2CH_2CH_2Cl}{|}}{C}HCH_2-$$

ClBu

Figures 1 and 2 show double-regression plots of eq 5 made with the Hjertberg–Sörvik[8] data. The [VC] values used for plotting were derived from the P/P_0 ratios in the way described elsewhere.[11] All of the reported[8] values of $\bar{\varrho}_{BB}$ have been included in these plots, with one exception, viz., the 45 °C value for a P/P_0 ratio of 0.61. In that particular instance, the correct value of [VC] could not be obtained from the pressure datum, for reasons that have been discussed.[12] The regression lines have been constrained to pass through the origin, as eq 5 requires, and their R^2 values (see figure captions) are satisfactory. Significantly, they exhibit no tendency toward upward curvature with increasing values of $[VC]^{-1}$. Thus they are quite consistent with the mechanism of eqs 1 and 2, and they constitute very strong evidence against diffusion control

Table 1. Dichlorobutyl Branch Concentrations in PVC

entry	polym type	polym temp, °C	[VC], M	$\bar{\varrho}_{BB} \times 10^3$ expt	$\bar{\varrho}_{BB} \times 10^3$ eq 9
1	suspension^a	82	4.85	2.4	1.2
2	suspension^b ($P/P_0 = 1.00$)	80	4.82	2.1	1.1
3	subsaturation^b ($P/P_0 = 0.59$)	80	1.94	4.4	2.8
4	bulk^c (sample V)	70	4.66	1.4^d	1.0
5	suspension^e (96% conv)	55	3.89	1.25^e	0.9
6	suspension^e (88% conv)	55	4.13	1.20^e	0.8
7	suspension^e (83% conv)	55	4.25	1.00^e	0.8
8	suspension^e (23% conv)	55	4.40	0.90^e	0.8
9	suspension^e (12% conv)	55	4.40	0.70^e	0.8
10	subsaturation^b ($P/P_0 = 0.92$)	55	3.39	1.6	1.0
11	suspension^c (sample VII)	54	4.39	1.2^d	0.8
12	suspension^a	40	~4.4	1.0	~0.6
13	solution^{e,f}	55	1.61^g (1.69)^h	2.75^e	2.1^i (2.0)^j
14	solution^{e,f}	55	1.40^g (1.55)^h	2.60^e	2.5^i (2.2)^j
15	solution^{e,f}	55	2.61^g (2.39)^h	2.20^e	1.3^i (1.4)^j
16	solution^{e,f}	55	1.76^g (1.76)^h	2.70^e	2.0^i (2.0)^j
17	solution^{e,f}	55	1.27^g (1.40)^h	2.55^e	2.7^i (2.5)^j
18	solution^k	40	4.61	0.9	0.5
19	solution^k	40	0.91	3.6	2.7
20	solution^k	40	0.46	5.6^l	5.4
21	solution^{m,n}	40	4.96	0.8^m	0.5

[a] Commercial resin. [b] Reference 12. [c] Reference 14. [d] Reference 15. [e] Reference 16. [f] 1,2,4-Trichlorobenzene solvent. [g] Calculated from conversion value determined[16] after solvent evaporation. [h] Calculated from conversion value determined[16] by polymer precipitation. [i] Calculated from the unparenthesized value of [VC]. [j] Calculated from the [VC] value in parentheses. [k] Reference 17; 1,2-dichloroethane solvent. [l] Value recalculated from Figure 2 of ref 10. [m] Reference 18. [n] VC–1,3-butadiene copolymer; 1,2-dichloroethane solvent.

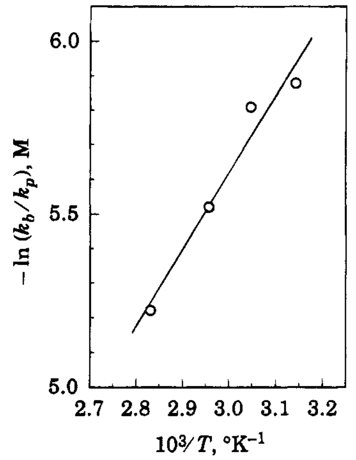


Figure 3. Plot of eq 8 ($R^2 = 0.96$) made with k_b/k_p values obtained from the plots in Figures 1 and 2.

of propagation within the [VC] ranges used. With recourse to a computational procedure that has been outlined previously,[11] we estimate that these [VC] ranges correspond to total conversions of ca. 83, 91, 89, and 88%, respectively, in ordinary bulk or suspension polymerizations conducted at 45, 55, 65, and 80 °C. From VC solubility data[8] and a published correlation of T_g with the PVC weight fraction in PVC–VC mixtures,[5b,d] we also find that these reaction temperatures are well above the T_g's of the VC-swollen polymer at the lowest [VC]'s used. Thus, in retrospect, the failure of these experiments to demonstrate diffusion-controlled propagation should not have been surprising.

A previous publication[11] reports other compelling evidence against propagation control by diffusion in the polymerization of VC. That evidence consists of linearity in plots of some rather complex equations which contain rate constants for several steps that are involved in the overall propagation reaction sequence.

The $(k_b/k_p) \times 10^3$ values obtained from the plots of eq 5 are 5.4, 4.0, 3.0, and 2.8 M, in the order of decreasing temperature. In Figure 3 these data are used in a plot of eq 8 from which values of A_b/A_p and $(E_b - E_p)$ can be extracted. Their substitution into eq 7 leads to eq 9.

$$\bar{\varrho}_{BB} \times 10^3 = (2800/[\mathrm{VC}])e^{-2200/T} \qquad (9)$$

The $(E_b - E_p)$ value turns out to be 4.4 kcal/mol, a result that verifies a qualitative prediction[12,13] that was made with regard to the relative magnitudes of E_b and E_p.

Comparison of Experimental and Predicted Values of $\bar{\varrho}_{BB}$. Table 1 lists experimental values of $\bar{\varrho}_{BB}$ for a variety of PVC specimens and compares them with $\bar{\varrho}_{BB}$ values obtained from eq 9. Except where noted otherwise, the experimental branch concentrations were determined during the present investigation. All of the polymers studied (except nos. 1 and 12; see below) were made at a constant temperature under conditions that allowed us to calculate the average concentrations of monomer during polymer preparation. These are the [VC] values that appear in column four. The experimental values of $\bar{\varrho}_{BB}$ were determined after dechlorination by using ^{13}C NMR, and they are believed to represent the sum of the Bu and ClBu concentrations in every case. For bulk and suspension polymerizations involving a transition from two organic phases to one, liquid monomer was assumed to vanish at 70% conversion,[19] and the saturation concentrations of VC in the polymer were obtained by data extrapolation, as described heretofore.[11] Since the conversions for polymers 1 and 12 were not available, the [VC] values used for these entries are the concentrations at saturation. If conversion is taken as 90% in both cases, eq 9 then gives $\bar{\varrho}_{BB} \times 10^3$ values of 1.3 and 0.6 for polymers 1 and 12, respectively. Monomer concentrations for entries 3 and 10 were determined in a previously outlined way,[11] and in the case of the polymers made in bulk, suspension, or with subsaturation, polymerization was assumed to have occurred exclusively in the monomer-swollen polymer phase.

Considering first the polymers that were not prepared in solution (entries 1–12), we note that, with few exceptions, eq 9 tends to give $\bar{\varrho}_{BB}$ values that are somewhat lower than those obtained by experiment. The reason for these discrepancies is not clear but may relate

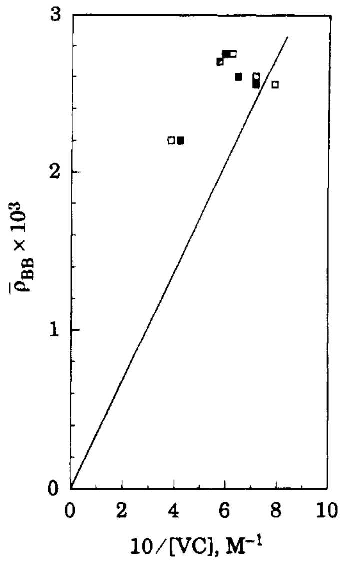


Figure 4. Plot of eq 5 made with data for entries 13–17 in Table 1. The slope of the line was obtained from eq 6, and the points were derived from experimental values that correspond to the conversions found[16] by (□) solvent evaporation, (■) polymer precipitation, and (◩) both methods.

to differences among the NMR procedures that were used by the various researchers who determined the $\bar{\varrho}_{BB}$ values. Interestingly, the experimental values of $\bar{\varrho}_{BB}$ seem unusually small for specimens 8 and 9, a result that implies the occurrence of significant amounts of monomer-phase polymerization for these low-conversion resins. If the $\bar{\varrho}_{BB} \times 10^3$ values found from eq 9 are simply multiplied by 1.5, the resultant set of data matches the values found by experiment (for entries 1–12) within an average deviation of ±0.2.

Equation 9 also tends to give rather low values of $\bar{\varrho}_{BB}$ for the polymers made in solution (entries 13–21). Here, however, the situation is somewhat confused, because the data[16] for entries 13–17 do not obey eq 5. This deficiency is demonstrated by the dispersion of the points in Figure 4. We cannot explain these results at present and are therefore forced to conclude that they may have resulted from the incursion of rather large experimental errors.

A clearer picture emerges from the values of $\bar{\varrho}_{BB}$ for entries 18–20. In Figure 5 these values have been used in a plot of eq 5 that has been compelled to intersect the origin, as in Figures 1 and 2. From the slope of this plot we find that $(k_b/k_p) \times 10^3$ is 2.7 M, a value in good agreement with the value of 2.5 M that can be obtained from eq 6 and the activation parameters determined from the plot in Figure 3. The close correspondence of these two values was not unexpected, in view of our other findings, and it reinforces the case against propagation control by diffusion, for the reasons given above.[20]

Conclusions

The $\bar{\varrho}_{BB}$ values of Hjertberg and Sörvik[8] for subsaturation PVC's comprise a self-consistent set of data that support the reaction mechanism of eqs 1 and 2. They also argue strongly against the occurrence of diffusion-controlled propagation during conventional polymerizations of vinyl chloride that are carried to high conversions. At temperatures ranging from 45 to 80 °C, the minimum conversion percentages to which this argument applies range from approximately 83 to 91, and they are insufficient to cause transformation of the monomer-swollen polymer into the glassy state. The absence of propagation control by diffusion at these conversions also is verified by the close similarity of some values of k_b/k_p for polymerizations carried out in the polymer phase and in dilute solution.

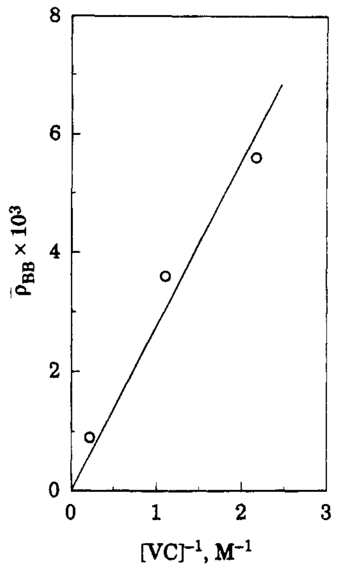


Figure 5. Plot of eq 5 ($R^2 = 0.97$) made with data for entries 18–20 in Table 1.

The Hjertberg–Sörvik data[8] have been manipulated to derive a relationship (eq 9) that can be used to predict the $\bar{\varrho}_{BB}$ values that pertain to various reaction conditions. Although the values thus found are somewhat lower, in general, than those determined by other workers, the discrepancies do not invalidate the major conclusions presented here, because those conclusions only require relative consistency, rather than absolute accuracy, of the $\bar{\varrho}_{BB}$ data on which they are based.

Experimental tests analogous to those described in the present paper can perhaps be used to probe for diffusion control of propagation in other systems where an intramolecular rearrangement competes successfully with the ordinary growth reaction.

Experimental Section

Reductive dechlorinations of PVC were performed by the usual two-stage procedure,[4,17] using dry THF and dry *m*-xylene as the solvents for the first and second stages, respectively. The $\bar{\varrho}_{BB}$ values determined by us that have not been reported previously were obtained from ^{13}C NMR spectra taken at 125.77 or 50.31 MHz. Procedural details for the NMR measurements were included in earlier publications.[3,4,10,17]

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(20) A reviewer wonders if some of the **1** radicals might be lost by H abstraction and/or C—C β scission. The relative importance of those reactions would be augmented by any factors that tend to reduce the rate of reaction 2, e.g., decreases in VC concentration and (perhaps) diffusion-controlled decreases in the rate constant for addition of VC to **1**. Reductions of $\bar{\varrho}_{BB}$ caused by losses of **1** would tend to lessen any upward curvature in the plots of eq 5 that was caused by diffusion control of k_p. However, the following analysis shows that side reactions of **1** were unimportant under the conditions of interest to us. At temperatures within the range studied here and at monomer conversions where diffusion control cannot be significant,[5b,d] no more than 0.2−0.3% of the propagating P$^\bullet$ radicals undergo the H abstractions that yield dichloro-*n*-butyl branches (see Table 1), long branches,[8] and internal double bonds.[12,13] A 3-fold reduction of [VC] (as in Figures 1 and 2), accompanied by a 10-fold decrease[5b,d] in the rate constant for reaction 2, would therefore lead to the loss of no more than ca. 6−9% of **1** by H abstractions, *if* the abstraction reactivities of **1** and P$^\bullet$ were comparable. In actual fact, transition-state steric hindrance and the greater thermodynamic stability of **1** should make its abstraction reactivity less than that of P$^\bullet$ and thus lead to losses of **1** by abstractions that are well below the 6−9% level under the conditions just described. Furthermore, the loss of **1** by C—C β scission would create some $-CH_2CCl{=}CH_2$ moieties at the ends of the polymer chains. We have never observed those end groups in PVC, although they should have been easy to detect in our ^{1}H NMR studies[12,13] or in our ^{13}C NMR examinations of Bu$_3$SnH-reduced PVC specimens.[4,10,17,21] When VC concentrations are very low, some of the **1** radicals apparently can be diverted into 1,3-diethyl and/or 2-ethyl-*n*-hexyl branch arrangements.[12,13] However, the losses of **1** occurring in that manner were too small to affect the conclusions of the present paper.[21]

(21) Starnes, W. H., Jr.; et al. To be published.

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