Molecular Microstructure of the Ethyl Branch Segments in Poly(vinyl chloride)

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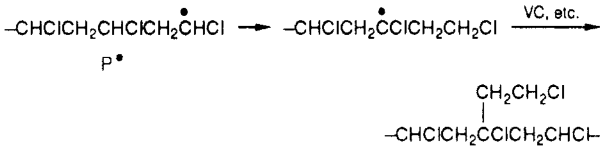
Received January 23, 1992; Revised Manuscript Received April 1, 1992

ABSTRACT: Carbon-13 NMR examination of reductively dechlorinated poly(vinyl chloride) at a field strength of 125.77 MHz reveals that the ethyl branches in the unreduced polymer are 1,2-dichloroethyl rather than 2-chloroethyl when the polymerization is carried out in an aqueous suspension at 40 or 82 °C. The 1,2-dichloroethyl moieties occur in a $-CHClCH_2CH(CHClCH_2Cl)CH_2CHCl-$ arrangement that results from a head-to-head emplacement of monomer and two successive 1,2 chlorine shifts. These shifts comprise a "billiard-ball" pathway for free-radical polymerization that apparently is without precedent.

Reductive dechlorination of poly(vinyl chloride) (PVC) with tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride, followed by ^{13}C NMR analysis of the "polyethylene" thus formed, has provided much information about the molecular architecture of PVC itself.[1] This information includes evidence for the presence of several branch structures whose concentrations lie in the following order: chloromethyl > 2,4-dichloro-*n*-butyl > 2-chloroethyl > long.[1,2] Tertiary halogen is thought to be present at the dichlorobutyl and chloroethyl branch points and at most of the long-branch points, as well.[1,2] For that reason, many workers have argued that these three branch points are important initiating sites for the thermal dehydrochlorination of PVC and thus are major contributors to the thermal instability of the polymer.[1b,2,3]

The occurrence of the 2-chloroethyl branch structure (1) has been intriguing for some time, because its apparent mechanism of formation (eq 1) involves the rearrangement of the macroradical, $P^\bullet$, via a 1,3 hydrogen transfer that requires a highly strained four-membered cyclic transition state.[2] Addition of vinyl chloride (VC) to the rearranged radical creates 1. Evidence for the chlorine substitution pattern of 1 has been provided by the ^{13}C NMR spectrum of a Bu_3SnD-reduced PVC sample that had been prepared by polymerization at 100 °C in bulk.[2] This spectrum was found to be consistent with the presence of the Et-*d* assemblage, shown in Figure 1, that would have resulted from the complete replacement of the chlorines in 1 by deuteriums.[2] The strongest spectral indication for branch structure Et-*d* was the greatly decreased intensity of the branch-point carbon signal vs that of the Et-br resonance (for nomenclature, see Figure 1) which had appeared in the spectrum of a Bu_3SnH-reduced sample of the same PVC.[2] Deuteration of the branch-point carbon was, in fact, expected to cause its resonance to vanish, owing to triplet splitting and to the unfavorable effects of deuteration on the NOE and T_1.[2,4] Nevertheless, the spectrum of the deuterated sample retained a small signal in the ethyl branch-carbon region.[2] This resonance was neither discussed in detail nor assigned. Even so, its appearance had evoked the possibility of the occurrence, in unreduced PVC, of another type of ethyl branch structure. From the NMR observations, it was apparent that such a structure would have to bear hydrogen rather than halogen on the branch-point carbon. Thus, unlike 1, if present, it would not be likely to be an effective initiator of thermal dehydrochlorination.


(1)

1

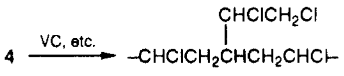
$$-CHClCH_2CHClCH_2\dot{C}HCl \;(P^\bullet) \longrightarrow -CHClCH_2\dot{C}ClCH_2CH_2Cl \xrightarrow{VC,\ etc.} -CHClCH_2\overset{\displaystyle CH_2CH_2Cl}{\overset{|}{C}}ClCH_2CHCl- \quad (1)$$

A possible route to this alternative branch structure has been described by one of us.[1a] This route involves four steps. The first two of these are head-to-head addition of monomer to the propagating macroradical (eq 2) and subsequent rearrangement of the ensuing radical, 2, via a 1,2 chlorine shift (eq 3). Both of these reactions were known to occur during VC polymerization, and the rearranged radical, 3, had been shown to be the immediate precursor of the chloromethyl branch arrangement.[5]

$$P^\bullet + VC \rightarrow \underset{\mathbf{2}}{-CHClCH_2CHClCHCl\dot{C}H_2} \quad (2)$$

$$2 \rightarrow \underset{\mathbf{3}}{-CHClCH_2CHCl\dot{C}HCH_2Cl} \quad (3)$$

$$3 \rightarrow \underset{\mathbf{4}}{-CHClCH_2\dot{C}HCHClCH_2Cl} \quad (4)$$


EB

(5)

$$4 \xrightarrow{VC,\ etc.} \underset{\mathbf{EB}}{-CHClCH_2\overset{\displaystyle CHClCH_2Cl}{\overset{|}{C}H}CH_2CHCl-} \quad (5)$$

The next step in the scheme[1a] was more conjectural. It involves yet another 1,2 Cl shift that transforms 3 into the doubly rearranged radical, 4 (eq 4). Addition of 4 to the methylene end of the monomer, followed by normal chain propagation, then generates the 1,2-dichloroethyl branch structure that we designate here as EB (eq 5). Its formation can be regarded as having proceeded via a modified "billiard-ball" route in which the first Cl that migrates is quickly replaced by another one.

The initial migration (eq 3) is strongly favored thermodynamically, because it converts a primary alkyl radical

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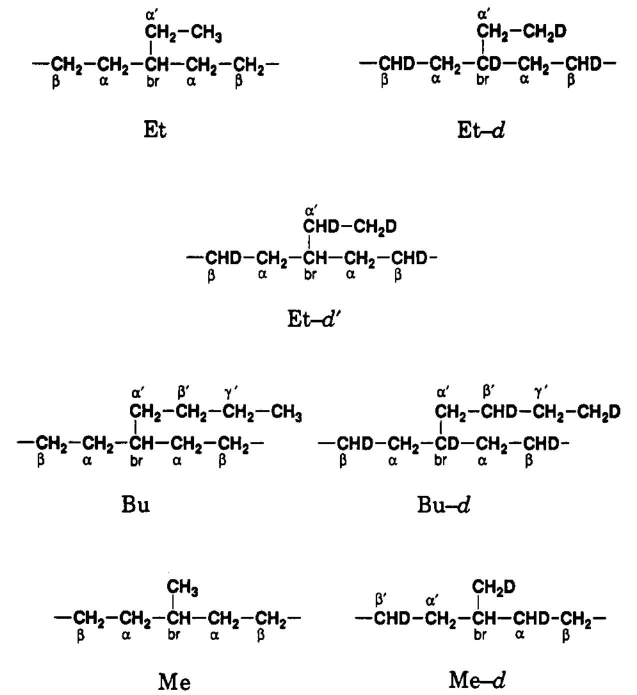

Figure 1. Possible short-branch structures in reduced PVC.

into a radical that is secondary and is, therefore, more stable. Thus this migration is very fast.[5,6] The second migration (eq 4), in contrast, involves a secondary-to-secondary radical transformation for which the energetics seem less advantageous.[1a,6] Hence, the occurrence of this reaction (and, thus, the ensuing EB formation) have remained problematical.

The product expected to result from the Bu_3SnD reduction of branch structure EB is the Et-*d*′ arrangement shown in Figure 1. Conclusive evidence for or against its presence, derived from ^{13}C spectra, has been unobtainable until recently, owing to its low concentration and to instrumental deficiencies in resolution and sensitivity. However, the advent of 125-MHz ^{13}C NMR instrumentation now has allowed these problems to be overcome. The present paper reports the use of such instrumentation and our reduction technique in order to establish the microstructure of the chlorinated ethyl branches in PVC that is made at commercial temperatures.

Results and Discussion

PVC Reduction and Structural Characterization. The PVC sample studied was a conventional suspension resin prepared at 82 °C, a temperature near the upper end of the commercial range.[1b,7] Separate portions of this polymer were reduced with Bu_3SnH or Bu_3SnD according to our standard method which has been described elsewhere.[2,8] Proton-decoupled ^{13}C NMR spectra of the reduced materials were then recorded at 125.77 MHz under essentially the same conditions (see the Experimental Section for details). Figures 2 and 3 show pertinent regions of the spectrum produced by the Bu_3SnH-reduced specimen, while Figure 4 contains portions of the spectrum of the Bu_3SnD-reduced material. In these figures the only resonances for which assignments are shown are those that relate directly to the ethyl branch structural problem. Both of the reductions were nearly complete, and in both cases the remaining amount of secondary halogen was only ca. 0.01 mol %, based on the integrated intensities of the very weak resonances of the $-CH_2CH_2CHClCH_2CH_2-$ or $-CHDCH_2CHClCH_2CHD-$ groups[2,8a,b,9] that were formed. In keeping with expectations evoked by earlier findings,[2] the complete spectrum of the Bu_3SnD-reduced sample contained no evidence for the occurrence of deuterium-scrambling reactions.

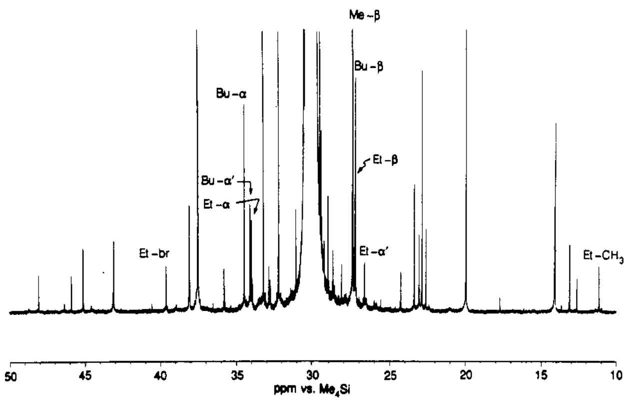

Figure 2. Proton-decoupled ^{13}C NMR spectrum (125.77 MHz) of Bu_3SnH-reduced PVC. The strong resonances near 19.9, 27.4, 30, 32.2, 33.2, and 37.5 ppm are shown in truncated form. Expanded versions of some resonances appear in Figure 3. For experimental details and nomenclature, see text and Figure 1.

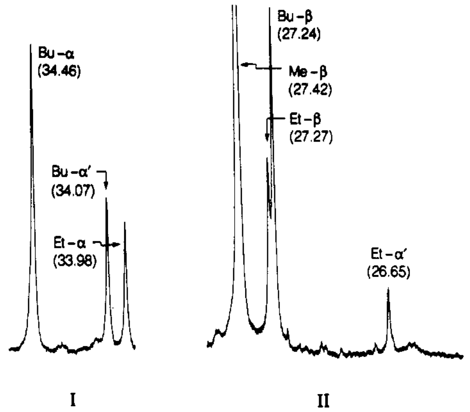

Figure 3. Expanded versions of some resonances appearing in the spectrum of Figure 2. Exact chemical shifts [(±0.05) ppm vs Me_4Si] are shown in parentheses.

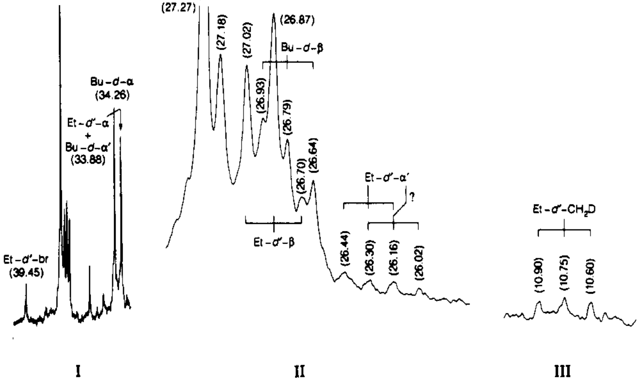

Figure 4. Proton-decoupled ^{13}C NMR partial spectra (125.77 MHz) of Bu_3SnD-reduced PVC. The strong resonances at 27.27 and ca. 37.4 ppm are shown in truncated form. Values enclosed in parentheses are exact chemical shifts [(±0.05) ppm vs Me_4Si]. For experimental details and nomenclature, see text and Figure 1.

Structural-defect concentrations were calculated from integrated peak intensities derived from all-inclusive versions of both of the carbon spectra. These concentrations then were used to determine those of the precursory structural defects in the unreduced PVC. The results obtained were as follows [structure, no. (±0.1) per 1000 C]: chloromethyl branch,[2,10] 2.9; 2,4-dichloro-*n*-butyl branch,[2,11] 1.2; ethyl branch structure(s), 0.5; long-

Table I
^{13}C Shifts of the Ethyl Branch Segments in Reduced PVC

	δ,[a] (±0.05) ppm vs Me_4Si			
carbon[b]	Bu_3SnH-reduced	Bu_3SnD-reduced	isotope shift,[c] ppm	deuteration pattern
Et-br (-*d′*-br)	39.60	39.45 (39.50)[d]	−0.15 (−0.10)[d]	1 neighbor
Et-α (-*d′*-α)	33.98	33.88	−0.10	1 neighbor
Et-β (-*d′*-β)	27.27	26.85[e,f]	−0.42[f]	1 attached
Et-α' (-*d′*-α')	26.65	26.30[e] (26.16)[e,g]	−0.35 (−0.49)[g]	1 attached, 1 neighbor
Et-CH_3 (-*d′*-CH_2D)	11.15	10.75[e]	−0.40	1 attached, 1 neighbor

[a] See the Experimental Section for details. [b] For nomenclature, see Figure 1. [c] Minus sign denotes upfield shift. [d] Value from another spectrum of the same sample. [e] Triplet center. [f] Estimated value; see text for discussion. [g] Possible alternative value; see text for discussion.

branch structure(s),[2] ≤0.1 (not detected[12]); internal allylic chloride,[13] 0.2; terminal allylic chloride,[14] 1.3; $-CH_2CHClCH_2Cl$ and $-CHClCH_2CH_2Cl$ long-chain ends,[2] 2.3; oxidized structures, ≤0.1 (not detected). These findings are in accord with expectations for a typical PVC specimen.[1,2]

Ethyl Branch Microstructure. The resonances of the Et structure are assigned in Figures 2 and 3, and their exact chemical shifts are given in the second column of Table I. The other resonances identified in Figures 2 and 3 are produced by the Bu and Me arrangements[2] that appear in Figure 1. Within the probable error limits, the tabulated shifts of the Et-br, Et-α, Et-β, and Et-CH_3 signals agree with values reported previously.[2,15] Coincident when observed at 50.31 MHz,[2] the Et-β and Bu-β peaks are partially resolved at 125.77 MHz (see part II of Figure 3), and their relative intensities strongly support the Et-β assignment.

The tabulated Et-α' shift is lower by 0.18 ppm than a value determined earlier[2] from another reduced PVC sample. However, this difference may simply reflect a minor inaccuracy in the earlier value, which was measured for a partially resolved weak signal in a region with considerable base-line drift.[2] In any case, Figure 3-II reveals that the 26.65 ppm resonance is the only Et-α' candidate.[17]

As we now will show, Figure 4 demonstrates conclusively that the Et-*d′* structure occurs in the Bu_3SnD-reduced polymer. This result obviously requires the presence of the EB segment in the starting PVC. It also establishes the mechanism of eqs 2–5, as no other reasonable route to structure EB is apparent.[18]

The exact chemical shifts of the Et-*d′* resonances are given in the third column of Table I. Most of these values are included in Figure 4, as well. This figure also contains some assignments and exact shift values for signals arising from the Bu-*d* and Me-*d* segments[2] that Figure 1 depicts. The fourth column of Table I shows the shift differences between the Et resonances and the corresponding Et-*d′* signals, while the fifth column describes the patterns of deuteration that have caused these differences to appear.

In Figure 4-I, the Et-*d′*-br resonance is a singlet, as required. Moreover, as anticipated, it has been shifted slightly upfield by the deuteron on a proximal carbon. The magnitude of the shift increment, 0.15 ppm, is somewhat greater than that expected on the basis of an earlier comprehensive study of reduced PVC.[2] However, further shift comparisons reveal that the increments found in that study[2] are lower, on the average, by about 0.06 ppm than those determined for the same resonances in the present investigation. Moreover, Table I shows that an upfield isotope shift of only 0.10 ppm was found for the Et-*d′*-br signal when the spectrum was redetermined.

Comparison of Figure 4-I with Figure 3-I demonstrates that the Et-*d′*-α carbons are nondeuterated and that each of them has only one deuterium neighbor. The Bu-*d*-α and Bu-*d*-α' carbons have two neighboring deuterons, and, as a result, their resonances have been shifted upfield by 0.20 and 0.19 ppm, respectively. On the other hand, comparisons of peak intensities reveal that the Et-*d′*-α and Bu-*d*-α' signals coincide at 33.88 ppm. Hence, the upfield isotope shift of the Et-*d′*-α resonance is only 0.10 ppm. This value is too low to have resulted from the attachment of more than one deuterium to the adjacent carbons.

The Me-*d*-β, Me-*d*-β', and Bu-*d*-β assignments made in Figure 4-II are supported by the peak intensities and by chemical shift predictions that were based on isotope shift increments and on the coupling constants expected for the resonances that are triplets.[2] Such considerations also indicate that the peak at 26.70 ppm must be the upfield branch of a triplet produced by the Et-*d′*-β carbons. If one makes the reasonable assumption[2,5,10] that the coupling constant for this triplet is 19 Hz, then its estimated chemical shift becomes 26.85 ppm.

The 26.0–26.5 ppm region of Figure 4-II establishes the presence of the deuterated Et-*d′*-α' carbon and shows that its triplet signal has a spacing of ca. 18 Hz, as expected. Nevertheless, the exact position of this triplet is somewhat uncertain. Peak intensities suggest that it is centered at 26.30 ppm. However, that designation requires a rather small isotope shift (see Table I) and leaves the 26.02 ppm resonance unassigned. The other possibility is that the center of the triplet lies at 26.16 ppm. In this scenario, the 26.44 ppm signal can be ascribed to the Et-*d*-α' carbon, and thus it now suggests the presence of a few 1 segments in the unreduced PVC. A choice between these interpretations cannot be made at this time.

The partial spectra shown in parts II and III of Figure 4 were plotted on the same scale. Thus the intensities of the peaks in these spectra can be compared directly. Such a comparison yields more support for the presence of the Et-*d′*-α' triplet by revealing that its intensity is similar to that of the Et-*d′*-CH_2D triplet assigned in Figure 4-III. The latter assignment is consistent with the observed isotope shift (see Table I) and with the observed coupling constant of about 19 Hz.

1,2-Dichloroethyl Branch Concentrations. For unreduced PVC, the fraction of chlorinated ethyl branches having the EB structure can be calculated from the relative intensities of the Et and Et-*d′* singlet resonances. By using integrated intensities obtained from the spectra of Figures 2–4, we find that the Et-*d′*-br/Et-br ratio is about 0.8, whereas the (Et-*d′*-α + Bu-*d*-α')/(Et-α + Bu-α') ratio is 1.0. Thus the EB structure comprised 80–100% of the ethyl branch segments in the unreduced PVC sample.

Similar intensity-ratio comparisons also have been made for resonances in the spectra of a suspension PVC specimen that had been prepared at 40 °C and then was reduced by us in a separate study.[19] These comparisons have indicated that, before reduction, all of the chlorinated ethyl branches in this polymer [0.2/(1000 C)] were of the EB type. Therefore, we conclude that this is certainly the predominant, if not the exclusive, ethyl branch structure in PVC that has been synthesized at temperatures within the normal commercial range. The unusual billiard-ball process by which this structure is made apparently has no precedent in the chemistry of free-radical polymerization.

The EB concentrations are, of course, rather low in comparison to those of some of the other structural defects in conventional PVC.[1,2] For that reason, one might be inclined to regard the EB formation as merely a minor aspect of the mechanism for the polymerization of vinyl chloride. To do so would be injudicious, for, as a subsequent paper[6] will show, the mechanistic implications of EB formation actually are of major significance.

Experimental Section

Materials. The PVC sample was supplied by B.F. Goodrich. It had been prepared by free-radical polymerization in an aqueous suspension at 82 °C, and its $\bar{M}_n$ and $\bar{M}_w$ were stated to be 1.9×10^4 and 3.9×10^4, respectively. Tri-*n*-butyltin hydride (Aldrich), tri-*n*-butyltin deuteride (Lancaster), and anhydrous *m*-xylene (Aldrich, No. 29,632-5) were used as received. Azobis(isobutyronitrile) (Pfaltz & Bauer) was recrystallized from methanol. Anhydrous THF (Aldrich, No. 18,656-2) was either used as received or refluxed with dipotassium benzophenone dianion under nitrogen overnight and then distilled under nitrogen immediately prior to use. Both types of THF gave good results in the reduction experiments. The other chemicals were purchased from various sources and had the highest purities that were available commercially.

Reductive Dechlorination of PVC. Reductive dechlorination with tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride was performed by following a two-stage procedure that closely resembled a published method.[2,8] (A procedure recommended by other workers[20] was not adopted, because it had been shown to give reductions that often were far from complete.[16,21]) Azobis(isobutyronitrile) was used for thermal initiation, and the solvents used in the first and second stages were anhydrous THF and anhydrous *m*-xylene, respectively. After precipitation into methanol, followed by Soxhlet extraction with methanol and subsequent drying, the reduced polymers required no further treatment before they were analyzed by NMR (cf. earlier studies in which additional purification to remove metallic residues had been required[2,8a,b]).

NMR Analysis. The pulse FT ^{13}C NMR spectra of the reduced PVC samples were recorded at 125.77 MHz with a Bruker AMX500 instrument using composite pulse proton decoupling, a 60° pulse with a width of 10 μs, a pulse repetition time of 10 s, a sweep width of 29 412 Hz, 64K data points, and a total spectral accumulation of ca. 2.3×10^4 scans. Samples were examined at 100 °C as 15% (w/v) solutions in ca. 4:1 (v/v) 1,2,4-trichlorobenzene/benzene-d_6 (for the Bu_3SnH-reduced polymer) or 1,2,4-trichlorobenzene/*p*-dioxane-d_8 (for the Bu_3SnD-reduced material), using hexamethyldisiloxane as an internal reference (2.00 ppm vs Me_4Si). Previous experience and concurrent studies with other reduced PVC samples had shown that the minor difference in solvent composition would have caused no significant changes in T_1's or chemical shifts.

Acknowledgment. We thank D. Skillicorn and F. J. Donat of the B.F. Goodrich Co. for supplying the PVC specimen and providing us with information about its properties and preparation. The research performed at the College of William and Mary was supported by the Polymers Program of the National Science Foundation under Grant No. DMR-8996253.

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(12) In Figure 2, the unassigned Bu-br resonance at 38.07 ppm has a weak downfield shoulder that might be ascribed to the branch-point carbon of a long-branch segment.[2] However, this assignment is not confirmed by peak integrations, which indicate a Bu-α/Bu-br intensity ratio of exactly 2.0.

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(17) Most of the unassigned resonances in Figure 2 have been discussed elsewhere.[2,5,8a,b,9,11,13,14,16]

(18) Copolymerization of VC with 3,4-dichloro-1-butene probably would produce the EB structure. However, to our knowledge, this dichloroalkene has never been found to be an impurity in a commercial VC monomer. It certainly was absent from the monomer used to make the PVC studied by us.

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