to a value of unity for the |tt| state in PP, which means that the |tt| conformation appears more frequently. The preponderance in the time-averaged conformational probability causes a more restricted segmental motion in the syndiotactic sequence than in the isotactic sequence in a PP chain. This tendency differs for the racemic dyad in PB, contrary to the case of the meso dyad. According to Flory,[14] there are additional unfavorable interactions between the ethyl group of the side chain and the chain backbone when both adjoining skeletal bonds are t, i.e., |tt|. The statistical weight of such interactions was assigned to τ^* (<1), which causes a decrease in the relative population of the |tt| conformation and an increase of the |gg| conformation. Thus, the ratio of the segmental motion of the syndiotactic sequence to that of the isotactic sequence decreases in PB as compared to PP.

Acknowledgment. We thank Mr. M. Ando for assistance in measuring the PP and PB NMR spectra.

Registry No. Atactic PP, 9003-07-0; isotactic PP, 25085-53-4; syndiotactic PP, 26063-22-9; isotactic PB, 25036-29-7.

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Branch Structures in Poly(vinyl chloride) and the Mechanism of Chain Transfer to Monomer during Vinyl Chloride Polymerization

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ABSTRACT: The detailed microstructure of poly(vinyl chloride) (PVC) has been determined from the ^{13}C NMR spectra of PVC samples that had been subjected to reductive dechlorination with tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride. From the information thus obtained and other pertinent facts, several important features of the vinyl chloride polymerization mechanism have been deduced. Investigation of a PVC specimen prepared in bulk at 100 °C has shown that 2,4-dichloro-*n*-butyl, 2-chloroethyl, and chlorinated long-branch segments are present and that all of these arrangements are tertiary-halogen-containing sites. The former structures are generated by free-radical "back-biting" routes, whereas the latter one appears to arise via chain transfer to the polymer by a growing-chain carbon radical. Identification of the long-branch points has been facilitated by the observation of a unique resonance for this grouping in the 50.31-MHz ^{13}C spectrum of reductively dehalogenated PVC. No evidence has been obtained for the occurrence of chlorinated *n*-propyl, *n*-amyl, 2-ethyl-*n*-hexyl, or 1,3-diethyl branch segments in PVC itself, but in keeping with our earlier findings, the presence of a chloromethyl branch structure containing tertiary hydrogen has been confirmed. For a series of PVC samples prepared at temperatures ranging from 43 to 100 °C, the branch concentrations have been demonstrated to lie in the following order: chloromethyl > 2,4-dichloro-*n*-butyl > 2-chloroethyl > long. The concentration data indicate that the activation energy for 2-chloroethyl branch formation is significantly greater than that for 2,4-dichloro-*n*-butyl branch production, an observation that may account for the failure of other workers to detect any ethyl branches in some samples of reductively dehalogenated PVC. In the case of the 100 °C bulk polymer, each number-average molecule has been found to contain one $-CHClCH_2CHClCH_2Cl$ long-chain end. The presence of this structure and the previously verified occurrence of chloroallylic long-chain ends in PVC are shown to establish the mechanism for chain transfer to monomer during the free-radical polymerization of vinyl chloride. This mechanism involves the addition, to the monomer, of an actual or incipient chlorine atom which results from the β scission of a chain-end radical that is formed via head-to-head monomer addition. The effect of tertiary halogen on PVC thermal stability is discussed, and earlier attempts to detect this grouping in the polymer are critically reviewed. Comments also are made with regard to the efforts of previous workers to identify the long-chain ends in PVC using NMR techniques. Finally, the presence of the $-CHClCH_2CHClCH_2Cl$ chain end is shown to rationalize much of the published chemical evidence for the existence of head-to-head linkages in the polymer.

Recent work in these laboratories has shown that reduction with tri-*n*-butyltin hydride can effect the essentially quantitative conversion of poly(vinyl chloride) (PVC) into the analogous hydrocarbon.[1,2] This method of reducing PVC is superior in many respects to the older lithium aluminum hydride procedure,[2a–d] and it has been shown to be a very valuable tool for use in PVC microstructure investigations in which the structure of the starting polymer is deduced from that of the reduction product.[1–3] The Bu_3SnH-reduced polymer has been characterized structurally with a variety of analytical techniques, including ^{13}C[1–3f,g,j–m] and ^{1}H[3k] NMR spectroscopies, IR spectroscopy,[2a,b,3b–e,h,i,n] pyrolysis–gas chromatography,[3a] pyrolysis–hydrogenation–gas chromatography,[3a,g,l] and γ-radiolysis–gas chromatography.[3d,h,n] However, ^{13}C NMR is clearly the method of choice for total structure determinations, since this technique provides the most information with mimimal ambiguity.

The present paper describes the results of ^{13}C NMR studies on polymeric alkanes that were prepared by reducing PVC with tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride. When the latter reagent was used, each chlorine

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atom was replaced by deuterium with no apparent scrambling of the label. Since the monodeuteration of a ^{13}C atom converts its proton-decoupled NMR signal from a singlet into a triplet and causes that signal, as well as those of neighboring carbons, to undergo upfield shifts,[1c,d,2e,4] it has been possible to identify the points of chlorine attachment in the original (unreduced) polymer by comparing the spectra of Bu_3SnH- and Bu_3SnD-reduced materials. This approach has allowed us to determine the complete constitutions of several PVC structural defects which incorporate various types of branches or are located at the ends of the polymer chains. Some of these defects undoubtedly have relatively low thermal stabilities; thus their identification has provided insight into the reasons for the thermal instability of PVC. In addition, this work and the results of some of our previous studies in this general area[1,2,4,5] have allowed us to specify, in reasonable detail, the mechanisms for propagation and chain transfer during the free-radical polymerization of vinyl chloride.

The present investigation was concerned primarily with a polymer prepared at 100 °C, a temperature somewhat higher than those used ordinarily for the commercial polymerization of vinyl chloride.[6] This temperature was selected in order to obtain concentrations of chain ends and branches that would be well within the detection limits of the 25.16-MHz spectrometer that was available for our initial studies. A potential disadvantage of this approach was the formation of appreciable amounts of anomalous structures that are unimportant for polymers that have been prepared at temperatures within the commercial range. Nevertheless, appropriate spectral comparisons showed that the major structural defects in several samples of commercial-type PVC were identical with those identified in our 100 °C specimen.

In the latter stages of the investigation, 50.31-MHz spectra were obtained. These spectra provided additional information which allowed us to extend the structural conclusions that had been drawn from the 25.16-MHz studies.

Results and Discussion

General Considerations. Tri-*n*-butyltin hydride reductions of simple alkyl chlorides (RCl's) are free-radical chain reactions whose propagation steps can be represented by eq 1 and 2.[7] Thus the structure of a particular re-

$$RCl + Bu_3Sn\cdot \rightarrow R\cdot + Bu_3SnCl \qquad (1)$$

$$R\cdot + Bu_3SnH \xrightarrow{k} RH + Bu_3Sn\cdot \qquad (2)$$

duction product, RH, can be correlated directly with that of its chloride precursor when $k[Bu_3SnH]$ is large enough to prevent competing R· reactions involving reorganization of the carbon skeleton or the creation of new functionality. This situation appears to obtain, for the most part, during Bu_3SnH reductions of PVC. Kinetic data for the Bu_3SnH reduction of a model *sec*-alkyl chloride, chlorocyclohexane,[8] suggest that the termination step of PVC reductions with Bu_3SnH involves $Bu_3Sn\cdot$ radicals almost exclusively under our experimental conditions. Thus the formation of anomalous structures via terminations involving R· should be unimportant in the PVC system. Indeed, we have obtained no NMR evidence for the presence of structures such as R–R and $RSnBu_3$, and evidence is also lacking for the incorporation of solvent moieties into the Bu_3SnH-reduced polymer. Rearrangement of R· by intramolecular hydrogen transfer will not change the final structure of the polymeric reduction product, nor will the final structure be affected by intermolecular hydrogen transfer from sources other than Bu_3SnH. In fact, we are aware of only one R· transformation that is capable of altering the carbon framework and can occur under our conditions at a rate which is comparable to that of reaction 2. This process is intramolecular 1,5 addition of the radical locus to an alkene double bond,[9] a reaction that leads to the formation of 1,2-dialkylcyclopentane moieties. Such moieties exist in Bu_3SnH-reduced PVC at many of the long-chain ends,[2e] and there are preliminary NMR indications for their occasional occurrence within the chains as well.[10] With these exceptions, it now would seem that, in view of the considerations just described, all of the structural defects found thus far in the Bu_3SnH-reduced polymer must have been derived directly from their chlorinated progenitors without rearrangement of the carbon skeleton.

In the case of Bu_3SnD reductions, the situation is potentially more complex, owing to the possibility of deuterium scrambling. Nevertheless, as will be discussed in subsequent sections, strong arguments against the occurrence of appreciable scrambling can be made from our spectral data. The deuterium kinetic isotope effect (k_{SnH}/k_{SnD}) for reaction 2 is certain to be rather small, since it has been reported to have values of only ca. 1.6–2.8 (at 25–80 °C) when R· is a simple alkyl radical.[8,11] Comparisons with published kinetic data for the Bu_3SnH reduction of chlorocyclohexane[8] suggest that an isotope effect within this range would not increase the R· concentration to an extent that would be sufficient to alter the predominant mechanism of radical-chain termination ($2Bu_3Sn\cdot \rightarrow$ inactive product)[8] under our reduction conditions. In keeping with this conclusion, no structures derived from R· termination have been detected by NMR in the Bu_3SnD-reduced polymer of the present study. The ^{13}C spectrum of this polymer also has given no unequivocal evidence for the presence of any groups derived from solvents, although, as expected, deuterated 1-ethyl-2-(long alkyl)cyclopentanes have been identified in this material.[2e]

With recourse to appropriate rate data for individual reaction steps, it is possible, at least in theory, to predict by calculation the amounts of solvent fragment incorporation and the extents of deuterium scrambling during our reductions of PVC. Calculations of this type have, in fact, been performed with data taken from ref 8 and 11a and several other sources of information that could be used to estimate the rates, at our experimental temperatures, of the R· reactions of interest (reactions with reducing agents and solvents and rearrangement by intramolecular hydrogen transfer). These computations were not quantitative in the strictest sense, owing to their dependence upon certain simplifying assumptions and to the possibility that the kinetic data of ref 8 are not directly applicable to reactions in aromatic and ethereal solvents.[12] Thus we will not attempt to present details of the calculations here and will simply note instead that they have predicted (a) no detectable incorporation of solvent fragments into the polymer and (b) deuterium scrambling amounting to only a few percent at most.

Preparation and Reduction of PVC. The principal objective of this study was the structural characterization of a laboratory sample of PVC that had been prepared in bulk at 100 °C using 1,1′-azobis(cyclohexanecarbonitrile) as a thermal radical source. One portion of this polymer was reduced in the usual (two-stage) way with Bu_3SnH.[2a,b] Another portion was reduced with Bu_3SnD in a similar manner, using a modified procedure that had been designed to prevent deuterium scrambling. The modifications introduced were (a) use of large excesses of the reductant during both reduction stages and (b) use of tetrahydrofuran rather than 2-methyltetrahydrofuran as the

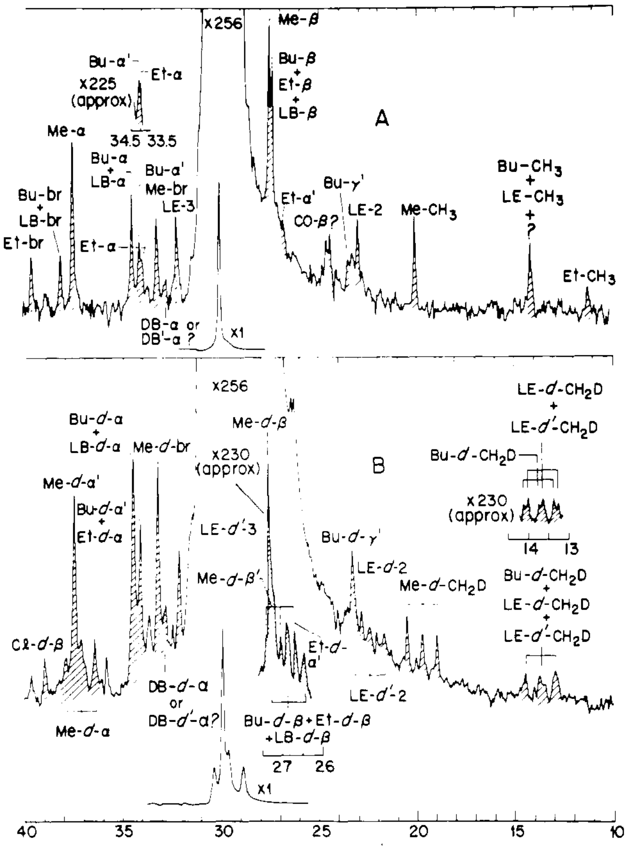


Figure 1. Proton-decoupled ^{13}C NMR spectra of PVC reduced with (A) Bu_3SnH or (B) Bu_3SnD. Traces designated as ×1 and ×256 were obtained at 25.16 MHz; partial spectra shown as insets were recorded at 50.31 MHz. For experimental details, nomenclature, and exact chemical shifts, see text, Figure 3, and Table I.

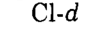
initial reduction solvent. (Kinetic data for reactions of methyl radicals with acyclic ethers[13] suggested that modification b would tend to retard the abstraction of solvent protium by polymeric carbon radicals.)

Proton-decoupled ^{13}C NMR spectra of the reduced samples are presented in Figure 1, where the B:A signal intensity ratio is roughly 2:1. Expanded versions of various resonances are displayed in Figure 2, which also contains partial spectra of the copolymer reference mixtures that are described in the following section. Figure 3 shows the completely reduced structures whose presence was established, while Table I contains the chemical shifts of all of the resonances that were assigned in the present study.

The downfield portions (not shown) of the 25.16- and 50.31-MHz spectra of sample A contain no resonance near 63.7 ppm that can be assigned to the Cl-α carbon of a Cl backbone structure.[2a,b] Since the estimated detection limit for this resonance is ca. 0.2/(1000 C), the Bu_3SnH reduction appears to have been ≥99.96% complete. In contrast, the spectra of sample B exhibit two weak signals whose chemical shifts[2a,b,5b] (Table I) and intensity ratio (approximately 1:2) are consistent with their assignment to the α and β carbons of a Cl-*d* arrangement. However, these resonances require the presence of only about 0.05 mol % of residual halogen.

$$-\overset{\gamma}{C}H_2\overset{\beta}{C}H_2\overset{\alpha}{C}HCl\overset{\beta}{C}H_2\overset{\gamma}{C}H_2-$$

Cl



$$-CHD\overset{\beta}{C}H_2\overset{\alpha}{C}HCl\overset{\beta}{C}H_2CHD-$$

Cl-*d*

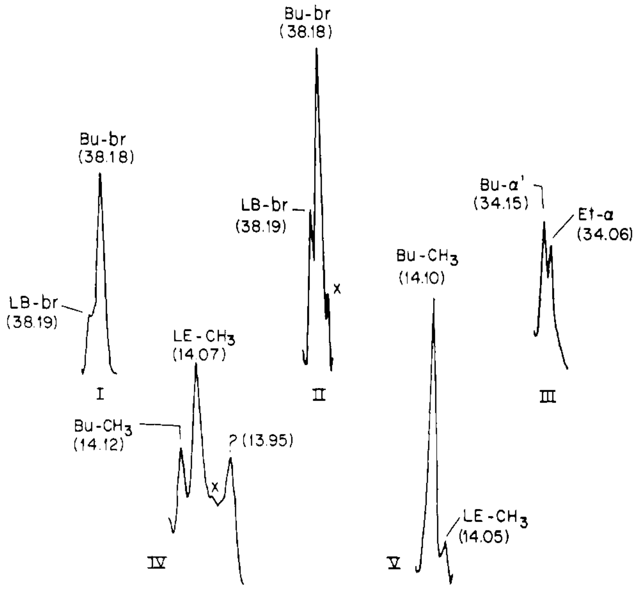


Figure 2. Expanded tracings of some composite resonances appearing in the proton-decoupled 50.31-MHz ^{13}C NMR spectra of (I) Bu_3SnH-reduced PVC, (II) a 2:1 ethylene–1-octene:ethylene–1-hexene copolymer mixture, (III and IV) Bu_3SnH-reduced PVC (cf. spectrum A of Figure 1), and (V) a 2:1 ethylene–1-hexene:ethylene–1-butene copolymer mixture (cf. Figure 4). Exact chemical shifts are shown in parentheses [ppm (±0.05) vs. Me_4Si]; signals marked with an "X" are thought to have resulted from instrumental noise. For experimental details and nomenclature, see text and Figure 3.

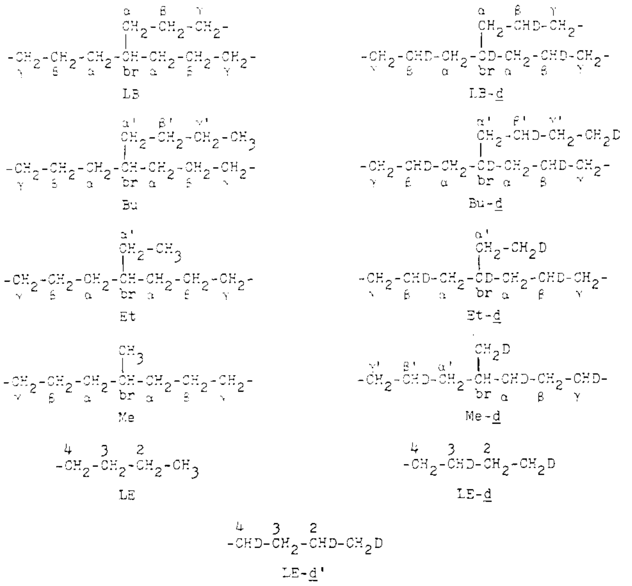


Figure 3. Completely reduced branch structures and saturated long-chain ends that have been identified in Bu_3SnH- or Bu_3SnD-reduced PVC using ^{13}C NMR.

In accordance with expectations, the lower trace of spectrum B consists of a singlet arising from the principal CH_2 carbons and an overlapping triplet produced by the principal CHD's. The ^{13}C–^2H coupling constant of the triplet has the anticipated value[4] of ~19 Hz, and the chemical shifts of both resonances (Table I) are in reasonable agreement with the values observed previously for other samples of poly(CH_2CHD).[4a,c,d]

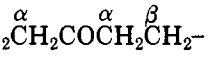
Spectrum B reveals no convincing evidence for the presence of oxygen-containing structures resulting from adventitious air oxidation. In contrast, spectrum A contains two resonances that have been assigned tentatively to the α and β carbons of a CO group [ca. 0.5 CO/(1000

Table I
^{13}C NMR Data for Reduced PVC

carbon	δ,[a] ppm vs. Me_4Si		isotope shift,[b] ppm	isotope substitution pattern
	Bu_3SnH reduced	Bu_3SnD reduced		
Cl-*d*-α		63.70^{c}		
Cl-*d*-β		39.03	-0.1^{d}	1 neighbor
CO-α	42.87^{e}			
CO-β	24.31^{f}			
LB-br	38.19			
LB-α	34.51			
LB-β	27.22			
LB-γ	$\sim 30.4^{g}$			
LB-*d*-α		34.38	−0.13	2 neighbors
LB-*d*-β		26.89^{h}	−0.33	1 attached
Bu-br	38.18			
Bu-α	34.51			
Bu-β	27.22			
Bu-γ	$\sim 30.4^{g}$			
Bu-α′	34.15			
Bu-β′	$29.55^{f,g}$ $(29.60)^{g,i}$			
Bu-γ′	23.35			
Bu-CH_3	14.12			
Bu-*d*-α		34.38	−0.13	2 neighbors
Bu-*d*-β		26.89^{h}	−0.33	1 attached
Bu-*d*-α′		34.00	−0.15	2 neighbors
Bu-*d*-γ′		23.21	−0.14	2 neighbors
Bu-*d*-CH_2D		13.79^{h}	−0.33	1 attached
Et-br	36.69			
Et-α	34.06			
Et-β	27.22			
Et-γ	$\sim 30.4^{g}$			
Et-α′	26.83^{g}			
Et-CH_3	11.07			
Et-*d*-α		34.00	−0.06	2 neighbors
Et-*d*-β		26.89^{h}	−0.33	1 attached
Et-*d*-α′		26.69	−0.14	2 neighbors
Me-br	33.25			
Me-α	37.52			
Me-β	27.38			
Me-γ	$\sim 30.4^{g}$			
Me-CH_3	19.95			
Me-*d*-br		33.13	−0.12	2 neighbors
Me-*d*-α		37.17^{h}	−0.35	1 attached
Me-*d*-β		27.28	−0.10	2 neighbors
Me-*d*-α′		37.50	−0.02	1 neighbor
Me-*d*-β′		27.05^{h}	−0.33	1 attached
Me-*d*-CH_2D		19.67^{h}	−0.28	1 attached
DB-α	$32.81^{f,g}$ $(32.88)^{g,i}$			
DB-*d*-α		$32.70^{f,g}$ $(32.82)^{g,i}$	−0.11 $(-0.06)^{j}$	1 neighbor
LE-CH_3	14.07			
LE-2	22.84			
LE-3	32.26			
LE-4	$29.60^{f,g}$ $(29.55)^{g,i}$			
LE-*d*-CH_2D		13.69^{h}	−0.38	1 attached
LE-*d*-2		22.71	−0.13	2 neighbors
LE-*d*′-CH_2D		13.69^{h}	−0.38	1 attached, 1 neighbor
LE-*d*′-2		22.40^{h}	−0.44	1 attached, 1 neighbor
LE-*d*′-3		32.06	−0.20	2 neighbors
principal CH_2	29.95	29.85	−0.10	2 neighbors
principal CHD		29.56^{h}	−0.39	1 attached

[a] Values obtained from traces shown in Figures 1 and 2 unless noted otherwise. Estimated accuracy, ±0.05 ppm. [b] Minus sign denotes upfield shift. [c] Appears in downfield region (not shown) of spectrum B, Figure 1. [d] Approximate value; cf. Cl—β shift in ref 5b. [e] Appears in downfield region (not shown) of spectrum A, Figure 1. Tentative assignment. [f] Tentative assignment. [g] Determined from 50.31-MHz trace (not shown). [h] Triplet center. [i] Possible alternative assignment. [j] Possible alternative value.

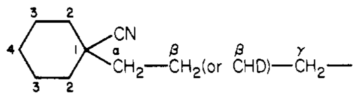
C)] on the basis of their chemical shifts[14] (Table I) and approximately equal intensities.



$$-\overset{\beta}{C}H_2\overset{\alpha}{C}H_2CO\overset{\alpha}{C}H_2\overset{\beta}{C}H_2-$$

CO

Both of the reduced specimens undoubtedly contained a few end groups that were derived from initiator radicals. If their nitrile function survived the reductions (as suggested by other studies[7b,15]), these groups should have appeared as structure 1. Theoretical maximum concen-



1

trations can be calculated for the carbons of 1 by assuming

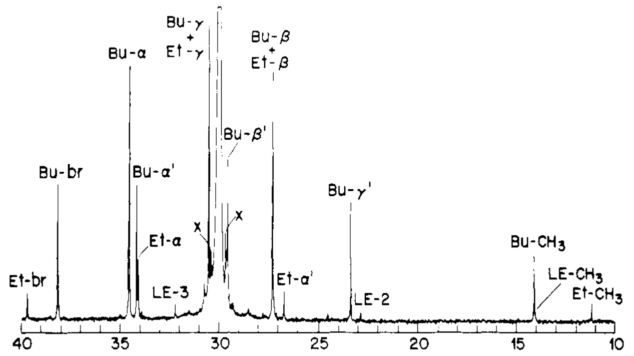


Figure 4. Proton-decoupled ^{13}C NMR spectrum (50.31 MHz) of a 2:1 ethylene–1-hexene:ethylene–1-butene copolymer mixture. Signals denoted by "X" are spinning side bands associated with the principal CH_2 resonance. For experimental details and nomenclature, see text and Figure 3.

that all of the initiator radicals were utilized (i.e., that there was no cage recombination of these radicals and no induced decomposition of the azonitrile) and that the rate constant for initiator decomposition was equal to its value in chlorobenzene at 100 °C (1.1×10^{-4} s^{-1}).[16] These assumptions and the polymerization data (Experimental Section) lead to calculated maxima of only 0.2/(1000 C) for the C-2 and C-3 carbons of the end group and 0.1/(1000 C) for its other carbons. Thus the ^{13}C resonances of 1 should not interfere significantly with those of the more important polymer defect sites. In order to verify this conclusion, a model compound for 1, 1-*n*-octylcyclohexanecarbonitrile, was prepared by alkylating cyclohexanecarbonitrile with 1-bromo-*n*-octane, and the ^{13}C NMR spectrum of the model was recorded under conditions essentially identical with those used for the polymer samples. With the aid of data for appropriate reference substances,[4c,d,17] all resonances of the model could be assigned, and in this way the chemical shifts of the carbons of nondeuterated 1 were found to be as follows [in ppm (±0.05) vs. Me_4Si]: C-1, 39.26; C-2, 36.30; C-3, 23.49; C-4, 26.02; C-α, 40.98; C-β, 24.76; C-γ (tentative assignment), 30.21; CN, 122.98.

Inspection of spectrum A shows that the relatively strong C-2 and C-3 resonances of 1 are absent; thus none of the other resonances in the spectrum are believed to have originated from an end group of this type. Spectrum B, on the other hand, contains small absorptions near some of the 1 positions, including a downfield resonance (not shown in Figure 1) at 40.90 ppm (the C-β triplet of deuterated 1 and the resonances of its C-1 and CN carbons would be extremely weak[4c,d,18] and are not observed). However, this evidence for the presence of 1 is not conclusive, and it will be seen from the following discussion that the occurrence of weak resonances arising from 1 would not affect our other arguments.

Copolymer Reference Spectra. In order to establish assignments for some of the resonances in Figure 1, the ^{13}C spectra of two mixtures of hydrocarbon copolymers were obtained for comparison purposes. Figure 4 depicts the 50.31-MHz spectrum of an ethylene–1-alkene copolymer blend.[1c] This blend contains *n*-butyl branches, ethyl branches, and saturated long-chain ends (i.e., the Bu, Et, and LE structures of Figure 3) at concentration levels of about 8.5, 1.6, and 1–2/(1000 C), respectively. The resonance assignments for these structures are based on published data[19] and on the relative peak intensities. Two aspects of Figure 4 are very interesting and significant; viz., the clear-cut separation of the Bu-α' and Et-α signals and the appearance of the LE-CH_3 resonance as a distinct shoulder on the Bu-CH_3 peak. The latter feature is revealed more clearly by spectrum V of Figure 2.

On the basis of earlier studies with poly(ethylene-*co*-1-alkenes),[19a,b] an *n*-hexyl branch point would appear to be an excellent model for the long-branch-point structure (LB) of Figure 3, insofar as the ^{13}C shifts of the backbone carbons are concerned (for our purposes, long branches are defined as those which have more than five carbons and produce the same LB resonances as a linear branch of infinite length). Spectrum II of Figure 2 shows an expanded 50.31-MHz version of the composite branch-point carbon resonance afforded by a mixture of ethylene–1-alkene copolymers containing *n*-hexyl and Bu branches. In this spectrum the branch-carbon signals are clearly resolved, and their origins are established by their relative intensities, which are reasonably consistent with the branch concentrations that the mixture was known to contain [*n*-hexyl = 1.7/(1000 C); Bu = 4.3/(1000 C)]. Our identification of a unique LB resonance[1c] provides a basis for the direct determination of LB structures in the presence of Bu and Et groups (in this connection, note the absence of any separate LB signal from spectrum A of Figure 1).

Structures Containing Tertiary Halogen. A. Previous Studies. Earlier attempts to find tertiary halogen in PVC have given conflicting results. Baum and Wartman[20] suggested that tertiary chloride was responsible for the residual thermal instability of PVC that had been subjected to dark chlorination in order to saturate double bonds. Inoue et al.[21] assigned a weak resonance in the ^{13}C NMR spectrum of unreduced PVC to methylene carbons adjacent to long-branch points containing tertiary halogen. This assignment was not supported by any reference spectral data. More recently, Braun and co-workers[3k,22] described some ^1H NMR observations that were originally said to indicate the presence of tertiary halogen,[22] a claim that has now been retracted.[3k]

Another approach to the problem was that of Bengough and Onozuka,[23] who carried out reactions of the polymer with cadmium acetate in the presence of pyridine and measured the extents of esterification by an IR technique. Their results, together with the results of parallel studies on model compounds,[23] suggested that appreciable amounts of tertiary chloride were present in PVC fractions having high molecular weights. However, a different conclusion was reached by Caraculacu et al.,[24] who endeavored to determine the total labile-halogen content of PVC (allylic plus tertiary chloride) by means of selective C–Cl phenolysis, followed by IR[24a,b] or UV[24c,d] measurement of the number of polymer-bonded phenolic groups. Model copolymers containing known amounts of tertiary chloride were used for calibration,[24,25] and the UV results were compared with those obtained by other methods that were believed to be specific for allylic halogen.[24c,d,26] These studies gave no evidence for the presence of tertiary halogen in PVC, and IR analysis of the polymer before phenolysis led to the same result.[24a] Nevertheless, in a very recent investigation, Buruiană et al.[27] found that phenol reacted with PVC that had been brominated in order to destroy allylic chloride groups, a result which was attributed to the presence of tertiary chloride sites.[27] However, this argument necessarily rests upon the tacit (and unverified) assumption that the structures formed by bromination were unreactive toward phenol.

Other investigations of the tertiary-halogen problem have involved comparative stability studies. Copolymers of vinyl chloride with 2-chloropropene[25,28] or 2,4-dichloro-1-pentene[24b] exhibit thermal stabilities which are much less than that of ordinary PVC[24b,25,28] and are related in an inverse manner to the extents of comonomer incorporation.[24b,25,28a,b,e,f] Since each of the comonomer units (except those introduced by chain transfer) should contain a branch carbon bearing halogen, these observations indicate that dehydrochlorination is initiated much more rapidly from such branch points than from the unactivated *sec*-C–Cl bonds of the vinyl chloride units.[24b,25,28] This conclusion is consistent with the results of liquid-phase dehydrochlorination studies on model compounds having low molecular weights.[25,29] Thus, if tertiary halogen were present at the branch points of PVC itself, one might expect to observe an inverse correlation between the branch-point concentration and the thermal stability of the polymer. However, several workers have reported that this correlation does not exist and that PVC stability is essentially unrelated to the total number of branches[29b,c,30] (in these studies, branch contents were estimated by IR[29b,c,30] or pyrolysis–gas chromatography[30d] methods after reduction with $LiAlH_4$). Such results have been taken as further evidence for the absence of tertiary halogen from most (or all) of the branch points in the polymer.[29b,c,30a,b]

The current work and our earlier NMR studies[1,2a–d,4,5] have now shown quite conclusively that the tertiary-halogen content of ordinary PVC is low and that the principal branch structure of the polymer [$-CHClCH(CH_2Cl)CH_2-$] does not contain tertiary halogen. Thus it is not surprising that other researchers have been unable to obtain convincing evidence for the presence of tertiary chloride with the alternative techniques described above. The insensitivity of these methods and their lack of specificity were recognized, in fact, by many of the workers who used them. With the aid of the technique applied in the present study, such difficulties can largely be overcome, and we now describe the use of this method in order to establish the presence of the various tertiary-halogen-containing structures that are discussed in the next three sections.

B. 2,4-Dichloro-*n*-butyl Branches. Spectrum A of Figure 1 provides conclusive evidence for the presence of the Bu structure of Figure 3. In the 25.16-MHz trace, the Bu-γ' resonance is clearly distinguishable, and this trace also contains a partially resolved resonance which can be assigned to the Bu-α' carbon with the aid of the reference spectrum in Figure 4. The Bu-α' signal is resolved more distinctly in the 50.31-MHz inset of spectrum A and in the expanded version of this inset which is shown in Figure 2 (partial spectrum III). In spectrum A, the Bu-CH_3 resonance appears as part of a composite signal which is found to contain three peaks when its 50.31-MHz trace is expanded (spectrum IV, Figure 2). Two of these peaks undoubtedly are associated with the Bu-CH_3 carbon and the LE-CH_3 carbon of the LE structure discussed below (see Figure 3), and it is clear from reference spectrum V of Figure 2 that the latter carbon resonates about 0.05 ppm upfield from the former one (a conclusion that has been further confirmed by the 50.31-MHz spectra of other reduced PVC samples having different Bu:LE ratios[31]). The assignments made for spectrum IV are based on this difference in chemical shifts, on the absolute shift values (cf. spectrum V), and on the relative intensities of the Bu-CH_3 and LE-CH_3 signals (cf. the relative intensities of the other Bu and LE resonances in spectrum A).[32] In Figure 1 the Bu-β' and Bu-γ resonances of spectrum A are obscured by the principal CH_2 signal. However, in the 50.31-MHz trace of the spectrum, two partially resolved signals (not shown) near 29.6 ppm can be assigned to the Bu-β' and LE-4 carbons, although it is not clear which resonance is which (studies with model compounds, including 9-*n*-butyl-*n*-heptadecane, have shown that the Bu-β' and LE-4 shift values are nearly identical under our conditions[31]). The 50.31-MHz spectrum also contains a strong resonance (not shown) near 30.4 ppm that evidently results from the Bu-γ carbons and the γ carbons of the other nondeuterated branch structures in Figure 3.[19a] Additional multicomponential resonances occur in spectrum A at the positions where the Bu-br, Bu-α, and Bu-β carbons should absorb, and it can easily be seen from relative intensity comparisons that the Bu-br and Bu-α carbons are the major contributors to their respective composite peaks. Moreover, the exact values of all of the Bu carbon shifts (Table I) are in good agreement with published data[19a] and with values obtained independently from the spectrum of Figure 4.

Spectrum B of Figure 1 reveals the presence of the Bu-d structure of Figure 3 and thus establishes the existence of 2,4-dichloro-*n*-butyl branches in the original polymer. The Bu-d-CH_2D carbon produces a 1:1:1 triplet signal which is partially resolved at 50.31 MHz and has the correct spacing[2e,4] (J_{CD}) of approximately 19 Hz. However, the Bu-d-γ' resonance appears as a singlet whose relative intensity is found to be identical with that of the Bu-γ' resonance of spectrum A when the presence of an underlying LE-d'-2 triplet component (discussed later) is taken into account. The composite signal containing the Bu-d-br triplet is too weak for detection, as expected,[4c,d,18] a result which actually comprises strong evidence for the presence of branch carbons bearing no protium. In contrast, the composite resonance that incorporates the Bu-d-β triplet is appreciably more intense, and two of its components can be identified ($J_{CD} \sim 20$ Hz, as anticipated[2e,4]) in the 50.31-MHz spectral trace. Not surprisingly, a composite singlet appears at the position where the nondeuterated Bu-d-α and LB-d-α carbons (see Figure 3) should absorb, but there is only one singlet in the region where the Bu-d-α' and Et-d-α resonances should occur, and these resonances also remain unresolved in the 50.31-MHz tracing (not shown). In the 34–35-ppm region of the 25.16-MHz trace of spectrum B, accurate intensity measurements are precluded by the occurrence of base line drift. However, the drift is negligible in this portion (not shown) of the 50.31-MHz scan. When comparisons are made between this tracing and the 50.31-MHz trace of spectrum A, the Bu-d-α + LB-d-α and Bu-α + LB-α resonances are found to have identical relative intensities, and the relative intensity of the Bu-d-α' + Et-d-α signal is seen to equal the sum of the relative intensities of the Bu-α' and Et-α peaks. Since the occurrence of the LB, LB-d, and Et-d structures of Figure 3 is conclusively established below, these results require the presence of the nondeuterated Bu-d-α and Bu-d-α' carbons, as well. These is no evidence for deuterium scrambling on any of the Bu-d carbons, in that the spectra show convincingly that each of these carbons bears exactly one deuterium or none (within the probable limits of error, which are ca. ±5–10%). Also, it is important to note that the isotope shifts of all of the detectable Bu-d resonances (Table I) are in keeping with the values predicted on the basis of related studies.[2e,4]

The chlorine substitution pattern of the *n*-butyl branch arrangement is consistent with the formation of this structure via a rearrangement of the growing-chain radical, **2**, into radical **3** by intramolecular hydrogen transfer (eq 3), followed by the addition of **3** to vinyl chloride in the conventional head-to-tail manner. Since the rearrangement step would compete with the reaction of **2** with monomer, the 2,4-dichloro-*n*-butyl branch concentration

$$\underset{\mathbf{2}}{\text{-CH}_2\text{CHClCH}_2\text{CHClCH}_2\dot{\text{C}}\text{HCl}} \rightarrow \underset{\mathbf{3}}{\text{-CH}_2\dot{\text{C}}\text{ClCH}_2\text{CHClCH}_2\text{CH}_2\text{Cl}} \quad (3)$$

of the polymer ought to increase with decreasing monomer concentration. Thus the proposed mechanism is strongly supported by our finding[5d] (to be reported elsewhere in detail[31]) of increasing numbers of Bu structures with decreasing concentrations of vinyl chloride for a series of Bu_3SnH-reduced samples of solution-polymerized PVC. Similar mechanistic evidence has been provided by other workers, who have used ^{13}C NMR to demonstrate the presence of relatively high concentrations of Bu groups in various Bu_3SnH-reduced PVC specimens that had been polymerized under monomer-starved conditions.[3f,j,k]

Studies using pyrolysis–hydrogenation–gas chromatography[3g,l] or γ-radiolysis–gas chromatography[3d,h,n,33] also have supported the occurrence of isolated *n*-butyl branches in reductively dehalogenated PVC. However, the chlorine substitution pattern of the halogenated Bu structure had not been determined directly prior to our preliminary account of this work.[1c]

C. Long-Branch Points. Previous ^{13}C NMR studies of poly(ethylene-*co*-1-alkenes) have shown that the br, α, and β carbon resonances of the LB structure in Figure 3 have chemical shifts that are very similar to those of the corresponding Bu signals.[19a,b] Thus it has been apparent to us for some time (and has been noted explicitly elsewhere[1b]) that the occurrence, now established, of Bu groups in reductively dehalogenated PVC would complicate the analysis for LB structures using ^{13}C NMR. Nevertheless, spectrum A of Figure 1 contains strong evidence for the presence of LB moieties and can be used to estimate their relative concentration.

Appropriate T_1 measurements[34] have shown that the Bu-br + LB-br and Bu-α + LB-α signal intensities in spectrum A can be compared quantitatively (with an error of ca. 3%). The latter intensity is greater than the former one by significantly more than a factor of 2. Thus the LB structure evidently does exist in the polymer sample, and from a more detailed intensity comparison, it follows that the LB and Bu concentrations of polymer A are about 0.3 and 0.9/(1000 C), respectively. The latter value agrees quite well [±0.1/(1000 C)] with the values obtained from the intensities of the Bu-α' and Bu-γ' signals when corrections are made for T_1 differences.[35]

Reference spectrum II of Figure 2 shows that the LB-br and Bu-br resonances can be observed as separate signals under favorable operating conditions. When the Bu-br + LB-br resonance of spectrum A was examined at 50.31 MHz with scale expansion, it also was split into two components, but this finding seemed inconclusive, owing to the low signal-to-noise ratio of the expanded trace. Nevertheless, splitting of the Bu-br + LB-br resonance has been observed convincingly with other samples of Bu_3SnH-reduced PVC, including the specimen affording partial spectrum I of Figure 2 (the original polymer used here had been prepared from a 1.0 M solution of monomer in 1,2-dichloroethane at 40 °C[5d,31]). The assignments for spectrum I are strongly supported by the intensities of the resonances[5d,31] as well as their chemical shifts (cf. the shift values for partial spectrum II). Splitting of the Bu-br + LB-br signal also has been demonstrated by Hjertberg and Sörvik,[3f,j] although these workers have provided no reference data to verify the LB-br assignment.

The LB arrangement conceivably could have arisen from several precursory structures containing halogen. One of these structures, corresponding to the LB-*d* grouping of Figure 3, would result from the conventional head-to-tail addition of monomer to a radical (**4**) formed by abstraction of hydrogen from an ordinary CHCl group of the polymer. A similar route involving radical attack on CH_2 would produce the intermediate species[36] **5** and lead to the halogenated grouping analogous to the LB-*d'* structure. Also, if the long-chain end **6** were present,[2e,4c,d] its copolymerization with vinyl chloride should yield the chlorinated counterpart of the LB-*d''* array.

$$\text{—CH}_2\text{CHClCH}_2\dot{\text{C}}\text{ClCH}_2\text{CHClCH}_2\text{—}$$

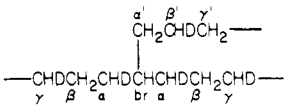
4

$$\text{—CHClCH}_2\text{CHCl}\dot{\text{C}}\text{HCHClCH}_2\text{CHCl—}$$

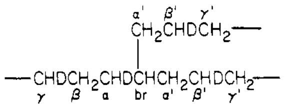
5

$$\text{—CHClCH}_2\text{CHClCH}{=}\text{CH}_2$$

6



LB-*d'*



LB-*d''*

In the preceding section of this paper, it was noted that the same relative intensity is observed at 50.31 MHz for the Bu-*d*-α + LB-*d*-α resonance of spectrum B and the Bu-α + LB-α resonance of spectrum A. This result can now be taken as evidence for the presence of the nondeuterated LB-*d*-α carbons in the deuterated polymer specimen. Furthermore, in spectrum B the LB-*d*-β resonance apparently comprises part of a composite triplet signal, as expected, and there are no indications in this spectrum (including the 50.31-MHz trace) for the triplet centered near 34 ppm or the singlet near 27 ppm that would be produced, respectively, by the α and β carbons of the LB-*d'* and LB-*d''* arrangements (the resonance at 27.05 ppm can be ascribed to another source, as discussed below). On the other hand, in the 50.31-MHz version of spectrum B, some absorptions (apparently singlets) that are only slightly above the noise level can be detected in the long-branch-point carbon region (38.0-38.2 ppm, not shown). These findings suggest that the long-branch points of polymer B are primarily of the LB-*d* variety. However, the NMR results per se do not entirely exclude the possibility that the LB-*d'* and LB-*d''* structures are present to some extent. Other arguments in favor of the LB-*d* structure will now be considered in detail.

First we address the question of whether the number of long-branch points is consistent with a mechanism involving hydrogen abstraction from the polymer (i.e., chain transfer to the polymer) by the growing-chain radical, **2**. This process would generate a saturated long-chain end whose reduction by Bu_3SnD would give the LE-*d* structure of Figure 3. Therefore, if such a mechanism were operative, the number of LE-*d* ends should be at least as large as the number of long-branch points in the polymer. This requirement is met in the case of sample B; in fact, it will be demonstrated in a later section that the LE-*d* concentration of this sample is about the same as its concentration of long-branch points. In theory, some of the **2** radicals could have acquired a hydrogen atom during transfer to the monomer or during a disproportionation process that terminated kinetic chains. However, the unsaturated long-chain ends that would have resulted from these reactions have not been detected in the present work or related studies,[1b,2,4,5] and hydrogen abstraction from the monomer certainly seems unlikely to have been able to compete effectively with hydrogen abstraction from the polymer, owing to the high strengths expected for the monomer's vinyl C–H bonds[37] and to the relatively low monomer concentration in the monomer-swollen polymer phase,[38] where most of the polymerization took place.[38b,39] Thus the concentration data for the LE-*d* ends and long-branch points of sample B suggest that the chlorinated analogues of both of these structures were formed primarily via a reaction of the polymer with radical **2**.

Would this process be likely to generate radical **4** in preference to **5**? Chain-transfer constants in the literature imply that the answer is yes. Values of the constant for transfer to polymer (C_P) have been estimated from the results obtained with transfer agents that can be regarded as models for PVC segments containing one, two, or three monomer units. These agents were, respectively, 2-chloropropane,[40] 2,4-dichloro-*n*-pentane,[41] and 2,4,6-trichloro-*n*-heptane,[41] and their respective C_P's (per monomer unit) at 50 °C have been reported to be 7×10^{-4},[40] 5×10^{-4},[41] and 5×10^{-4}.[41] The growing-chain radical, **2**, was probably the major attacking species involved in the reactions to which these data refer, and chlorine-atom abstraction by such a radical is unlikely to be important in these systems.[42] Furthermore, hydrogen abstraction by **2** from sites other than CHCl should have caused the C_P for 2-chloropropane to be appreciably lower than the other C_P values, owing to the low reactivity of primary hydrogens toward attack by carbon radicals.[13,42] Thus, if the C_P's of the models are accepted at face value, their close similarity can be taken as evidence for the preferential abstraction, by radical **2**, of CHCl hydrogen in all three cases. This result is not unreasonable, for an α-chloro substituent is known to enhance the reactivity of C–H hydrogen toward other carbon radicals (trifluoromethyl,[43] poly(tetrafluoroethyl),[44] cyclohexyl,[45] and polyethyl[46]) encompassing a wide polarity range.

In light of the preceding discussion, it now seems reasonable to conclude that the chlorinated LB-*d* analogue is, indeed, the principal type of long-branch point in our 100 °C PVC specimen, and that this structure did result primarily from a chain-transfer reaction of radical **2**. Additional ^{13}C NMR studies of this problem, performed at a higher field strength, would probably be worthwhile.

D. 2-Chloroethyl Branches. The spectra of Figure 1 also establish the presence of isolated 2-chloroethyl branches in our 100 °C PVC sample. Upon reduction with Bu_3SnH, the polymer segments containing these branches are converted into the Et arrangement of Figure 3. In spectrum A, the Et-CH_3, Et-α', Et-br, and Et-α resonances all appear as separate peaks (see also spectrum III of Figure 2), while the Et-β resonance overlaps with the Bu-β and LB-β signals, as expected[19] (cf. Figure 4). The measured Et shifts (Table I) are in good accord with Randall's values,[19a] as well as those determined from Figure 4, and the relative intensities of the Et-CH_3, Et-α', Et-α, and Bu-β + Et-β + LB-β absorptions (corrected for T_1 differences)[34,35,47] are resonably consistent with the assignments made. On the other hand, the Et-br intensity is somewhat greater than required.

The spectrum of polymer B confirms the formation of the Et-*d* group of Figure 3. Since no peaks appear in the 11-ppm region of this spectrum, the methyl group of the ethyl branch must now contain deuterium. The Et-*d*-α' singlet evidently coincides with the upfield component of the Me-*d*-β' triplet discussed below, since this component is much more intense than expected on the basis of the base line drift (cf. the relative intensities of the Bu-*d*-β + Et-*d*-β + LB-*d*-β triplet components). Significantly, the resonance at the ethyl branch-point carbon position is much weaker in spectrum B than it is in spectrum A. This decrease represents a concentration loss of about 1.0/(1000 C), a value in reasonable agreement with the Et branch content of polymer A. Thus the branch-point carbon must now be deuterated, and the abnormally high intensity of its resonance in spectrum A must have resulted from the incursion of the overlapping, unidentified signal that remains in spectrum B. Relative intensity data discussed in an earlier section are consistent with the presence of the Et-*d*-α carbons in sample B, while the occurrence of the Et-*d*-β triplet as part of a composite signal is in keeping with the anticipated isotope shift.[2e,4] The Et-*d*-α and Et-*d*-α' assignments also are supported by the isotope shift data in Table I,[4] and there are no indications for deuterium scrambling on any of the Et-*d* carbons.

The 2-chloroethyl branch structure is believed to have been formed via a "back-biting" reaction (eq 4) analogous

$$\mathbf{2} \rightarrow \underset{\mathbf{7}}{-\mathrm{CH_2CHClCH_2\dot{C}ClCH_2CH_2Cl}} \qquad (4)$$

to eq 3, followed by a head-to-tail addition of the product radical (**7**) to the monomer. Percipient readers may have realized already that the chlorinated Et-*d* analogue would also ensue from the head-to-tail copolymerization of vinyl chloride with 2,4-dichloro-1-butene. Indeed, an homologous substance, 2,4-dichloro-1-pentene, has been reported to copolymerize with vinyl chloride[24b,26,48] in this way.[24b,26] However, to our knowledge, 2,4-dichloro-1-butene has never been discovered to be an impurity in commercially synthesized vinyl chloride,[49] and this alkene could not be detected by gas chromatography–mass spectrometry (GC–MS) in our original stock of monomer or in the monomer fractions that were recovered from our polymerization experiments. Other GC–MS analyses showed that the halogenated butene was not produced when vinyl chloride and anhydrous HCl were heated at 100 °C for several hours in the absence of a radical source. Thus the copolymerization route to the 2-chloroethyl branch structure seems most improbable at this time.

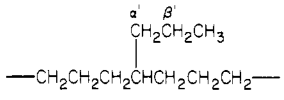
The presence of 2-chloroethyl branches in PVC has not been demonstrated by other workers. Using IR,[50] ^{13}C NMR,[3f,j,k,51] or γ-radiolysis followed by the analysis of volatile products,[3d,h,33,52] many other investigators have obtained no conclusive evidence for the occurrence of ethyl branches in the reductively dehalogenated polymer. In the case of the unreduced polymer, the existence of 2-chloroethyl branches was formerly thought to be supported by some ^1H NMR data[22] that are now considered to be ambiguous.[3k] Nevertheless, in keeping with our observations, pyrolysis–hydrogenation–gas chromatography work[3a,g,1,53] and a very recent γ-radiolysis–gas chromatography study[3n] have indicated the presence of low concentrations of ethyl branches in various reduced PVC specimens.

In a subsequent section of this paper, we discuss a plausible reason for the apparent absence of 2-chloroethyl branches from some samples of PVC.

Chloromethyl Branches. Previous work in these laboratories has shown that the most abundant short-branch grouping in ordinary PVC is the chlorine-containing counterpart of the Me-*d* structure in Figure 3.[1b,2a–d,31,4a,b,5] Reduction with Bu_3SnH should convert the chloromethyl branch arrangement into the Me structure of Figure 3 and, as expected, the Me-CH_3, Me-br, Me-α, and Me-β resonances all appear at their correct shift positions[4a,c,d,19a] and relative intensities in spectrum A of Figure 1. In spectrum B, the tripartite Me-*d*-CH_2D, Me-*d*-α, and Me-*d*-β' signals can easily be detected (with $J_{CD} \sim 19$ Hz, as anticipated[2e,4]), although the upfield component of the last two triplets is obviously somewhat enhanced. It was pointed out in the preceding section that the enhancement observed in the Me-*d*-β' case can be accounted for by the presence of an overlapping Et-*d*-α′ absorption. Spectrum B also contains singlets that can be assigned to the Me-*d*-br, Me-*d*-α′, and Me-*d*-β carbons. These resonances appear at mutually comparable strengths in the complete 50.31-MHz trace (not shown), and their isotope shifts, as well as those of the other Me-*d* signals (Table I), are in satisfactory agreement with expectations.[2e,4] Moreover, intensity comparisons made among the various traces of spectra A and B show that the Me and Me-*d* contents of the two reduced specimens are essentially equivalent [±0.1/(1000 C)]. Thus all of the spectral data are consistent with the presence of the chlorinated Me-*d* analogue in the starting polymer, and again there is no evidence for deuterium scrambling during the reduction with Bu_3SnD.

The chloromethyl branch structure of PVC is formed by a mechanism involving head-to-head addition of monomer to the growing-chain radical, **2**, followed by a 1,2 shift of a chlorine atom and subsequent head-to-tail propagation.[4c,d] Some important ramifications of this scheme are discussed below in the section that deals with the mechanism of chain transfer to the monomer.

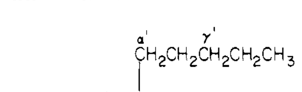
Other Possible Branch Structures. A. Chlorinated *n*-Propyl Branches. According to Randall's ^{13}C NMR data for poly(ethylene-*co*-1-alkenes),[19a,54] the presence of the isolated *n*-propyl (Pr) branch structure in reductively dehalogenated PVC should be revealed by the appearance of unique resonances at ca. 14.6, 20.3, and 36.8 ppm, corresponding to the Pr-CH_3, Pr-β′, and Pr-α′ carbons, respectively.[55] Neither of these resonances can be detected in spectrum A of Figure 1, nor is there any observable absorption at 20.85 ppm, which is the chemical shift ascribed to the Pr-β′ signal by other workers.[56] Thus there is no evidence for the presence of chlorinated *n*-propyl branches in the original 100 °C PVC sample. Other investigations of reduced PVC using a variety of analytical techniques also have given no firm indications for the occurrence of isolated *n*-propyl groups.[3a,d,f-h,j-l,n,33,51,53]



$$-CH_2CH_2CH_2\underset{}{C}H(\overset{\alpha'\ \ \beta'}{CH_2CH_2CH_3})CH_2CH_2CH_2-$$

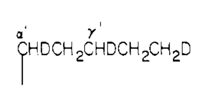
Pr

B. Chlorinated *n*-Amyl Branches. Studies by Randall[54] and other workers[19b,56] have shown that the Am structure depicted above will produce an Am-γ′ resonance at 32.7–32.8 ppm. In fact, the 25.16-MHz trace of spectrum A contains a composite signal near this region which, when examined at 50.31 MHz, is found to consist of two peaks whose exact shift values are 32.88 and 32.81 ppm.[2e,10] One of these resonances (probably the former one) arises from a dialkylcyclopentane moiety that was created by the reduction process,[2e,10] but the other peak has not been assigned thus far, and its presence therefore allows one to entertain the possibility that the Am structure is present. However, if chlorinated *n*-amyl branches were formed in the starting polymer via eq 5 and subsequent addition of monomer (which seems to be the only plausible route), these branches should have been converted into Am-*d* groups by Bu_3SnD. Since the Am-*d*-γ′ carbon is deuterated, its resonance should either be undetectable or appear as a very weak triplet which is shifted upfield from the Am-γ′ position by ca. 0.3–0.5 ppm[2e,4] (cf. the isotope shifts in Table I). Yet spectrum B retains two resonances at 32.70 and 32.82 ppm (values taken from the 50.31-MHz trace[2e,10]) whose relative intensities are about the same as those of the 32.81- and 32.88-ppm signals of spectrum A.[2e,10] Furthermore, if a significant number of Am-*d* groups were present in sample B, the relative intensity of the resonance designated as Bu-*d*-α + LB-*d*-α would be appreciably less than that of the Bu-α + LB-α signal of spectrum A, in contrast to the experimental observation (see above). This conclusion follows from the realization that both the Am-α and Am-α′ resonances would contribute to the Bu-α + LB-α intensity,[19a,b,54,56] and that this contribution would be reduced by ca. two-thirds in the Bu-*d*-α + LB-*d*-α case, owing to the presence of deuterium on the Am-*d*-α and Am-*d*-α′ carbons. In view of these considerations, we believe that the PVC sample now under discussion contained few, if any, branches of the chlorinated *n*-amyl variety. This finding is consistent with the results of other structural studies on reductively dehalogenated PVC.[3a,d,f-h,j-l,n,33,51-53]



$$-CH_2CH_2\underset{\alpha}{C}H_2\underset{}{C}H(\overset{\alpha'\ \ \ \gamma'}{CH_2CH_2CH_2CH_2CH_3})\underset{\alpha}{C}H_2CH_2CH_2-$$

Am



$$-CHDCH_2\underset{\alpha}{C}HD\underset{}{C}H(\overset{\alpha'\ \ \ \gamma'}{CHDCH_2CHDCH_2CH_2D})CH_2CHDCH_2-$$

Am-*d*

$$2 \rightarrow -CHClCH_2CHCl\dot{C}HCHClCH_2CHClCH_2CH_2Cl \quad (5)$$

8

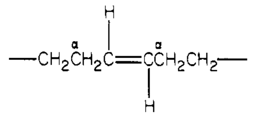
Several ^{13}C NMR investigations have suggested that low-density polyethylene (LDPE) does contain an appreciable number of Am structures.[1d,3d,5a,c,19a,b,54,56,57] These groups presumably would have to be formed via a 1,6 hydrogen-transfer reaction analogous to eq 5, and such a process is indeed known to occur with smaller *n*-alkyl radicals at a rate that allows it to compete successfully with 1,5 hydrogen migration[9e,58] (cf. eq 3; with 1-*n*-undecyl radical, for example, the ratio of 1,5 to 1,6 hydrogen transfer is about 3 at 69–125 °C[59]). Hence the absence of chlorinated *n*-amyl branches from PVC demands an explanation.

A property that probably intervenes here is relative radical stability. All "back-biting" reactions of unsubstituted *n*-alkyl radicals involve primary-to-secondary radical conversions. Thus these reactions are exothermic. Reactions 3 and 4 should be exothermic, as well, since they involve primary-to-secondary conversions in which both the starting and product radicals are stabilized by α-chloro substitution. On the other hand, in the case of reaction 5, only the starting radical is stabilized in this way. Hence this reaction should be much less exothermic than reactions 3 and 4, and it may even be endothermic.[4c] In either event, it is clear that the tendency of **2** to rearrange by 1,6 hydrogen transfer is disfavored by a thermodynamic factor which is inoperative in the unsubstituted *n*-alkyl radical case. The same factor favors the preferential formation, discussed above, of radical **4** as compared to **5**. (However, we recognize, of course, that in general, the relative rates of competing radical reactions are not determined exclusively by the thermodynamic stabilities of the radicals that are involved.)

Another conceivable reason for the absence of chlorinated *n*-amyl branches is that radical **8** is destroyed by β scission (eq 6) before its addition to monomer occurs. This possibility can neither be established nor disproven with the information now on hand. Nevertheless, it should be noted that the "extra" resonance near 32.8 ppm in the spectra of Figure 1 can be assigned to carbons that are α to internal trans double bonds.[2a-d,4,60] These linkages could be situated well within the polymer backbone (as in the

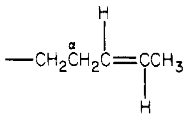
$$-CHCl\dot{C}HCHCl- \rightarrow -CH{=}CHCHCl- + Cl\cdot \quad (6)$$

DB and DB-*d* structures), or they could be in the penultimate position of some of the long-chain ends (i.e., in DB′ and DB-*d*′ groups[2e,10]).[61] If the DB and DB-*d* structures are assumed to be the ones that actually are present, their concentrations can be estimated to be about 0.3 and 0.5/(1000 C), respectively, from the spectral results.



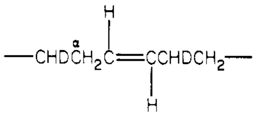
$-CH_2\overset{a}{C}H_2\overset{H}{C}=\underset{H}{C}\overset{a}{C}H_2CH_2-$

DB



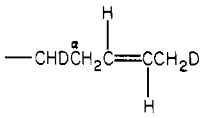
$-CH_2\overset{a}{C}H_2\overset{H}{C}=\underset{H}{C}CH_3$

DB′



$-CHD\overset{a}{C}H_2\overset{H}{C}=\underset{H}{C}CHDCH_2-$

DB-*d*

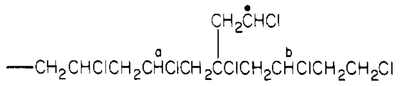


$-CHD\overset{a}{C}H_2\overset{H}{C}=\underset{H}{C}CH_2D$

DB-*d*′

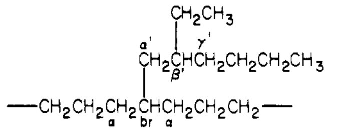
In a subsequent paper,[10] the question of internal unsaturation in PVC will be examined in more detail.[62]

C. Chlorinated 2-Ethyl-*n*-hexyl and 1,3-Diethyl Branches. Willbourn[64] has described a "double-back-biting" mechanism that could lead to the formation of 2-ethyl-*n*-hexyl or 1,3-diethyl branch structures during the free-radical polymerization of ethylene. An analogous scheme can be envisaged for the vinyl chloride system. In this case the mechanism would involve the occurrence of reaction 3, followed by the incorporation of a single monomer unit into the product radical. The resultant species, **9**, could then rearrange by 1,5 hydrogen transfer in either of two ways. Migration of hydrogen "a" and subsequent addition of monomer would produce a chlorinated 2-ethyl-*n*-hexyl branch-containing segment that should appear as an EtHe structure after reduction with Bu_3SnH, or as an EtHe-*d* structure upon reduction with Bu_3SnD. Alternatively, transfer of hydrogen "b", followed by monomer incursion, would generate a 1,3-bis(2-chloroethyl) grouping whose reduction should yield a DiEt or DiEt-*d* arrangement.



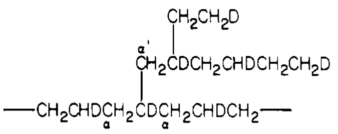
$-CH_2CHClCH_2\overset{a}{C}HClCH_2\overset{CH_2\dot{C}HCl}{C}ClCH_2\overset{b}{C}HClCH_2CH_2Cl$

9



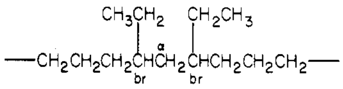
$-CH_2CH_2\underset{a}{C}H_2\underset{br}{\overset{\overset{a'}{C}H_2\underset{\beta'}{\overset{CH_2CH_3}{C}}H\overset{\gamma'}{C}H_2CH_2CH_2CH_3}{C}}H\underset{a}{C}H_2CH_2CH_2-$

EtHe



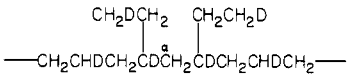
$-CH_2CHD\underset{a}{C}H_2\overset{\overset{a'}{C}H_2\overset{CH_2CH_2D}{C}DCH_2CHDCH_2CH_2D}{C}D\underset{a}{C}H_2CHDCH_2-$

EtHe-*d*



$-CH_2CH_2CH_2\underset{br}{\overset{CH_3CH_2}{C}}H\overset{a}{C}H_2\underset{br}{\overset{CH_2CH_3}{C}}HCH_2CH_2CH_2-$

DiEt



$-CH_2CHDCH_2\overset{CH_2DCH_2}{C}D\overset{a}{C}H_2\overset{CH_2CH_2D}{C}DCH_2CHDCH_2-$

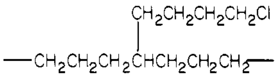
DiEt-*d*

Calculations using different sets of empirical parameters have predicted that the EtHe-br and EtHe-α resonances will appear in the 34.7–35.5-ppm region,[19b,56] and a weak absorption has, in fact, been detected at 34.7 or 34.8 ppm in the ^{13}C spectra of various LDPE's.[3d,56,57b] In contrast, there are no distinct signals at 34.7–35.5 ppm in spectrum A of Figure 1, nor is there any resonance in spectrum B that can be assigned to the EtHe-*d*-α carbons. Other weak LDPE resonances have been observed at 37.2 ppm[56] or at 37.0 and 37.4 ppm.[3d,57b] Calculations suggest that they could arise from the EtHe-β'[3d,19b,56,57b] and EtHe-γ' carbons,[56] yet they also are absent from spectrum A (even at 50.31 MHz). The EtHe-α' absorption has been predicted to occur at 38.7–38.8 ppm[19b,56] and is thought to have been detected experimentally at 38.9 ppm in some LDPE spectra.[3d,56,57b] A weak signal does appear at ca. 38.9 ppm in the 25.16-MHz trace of spectrum A, but it is not visible in the 50.31-MHz trace and thus is presumed to be an artifact. Furthermore, even if this peak were real, it could not be ascribed to the EtHe-α' carbon, as there is no unassigned resonance in the region of spectrum B where the EtHe-*d*-α' signal should appear (ca. 38.7–38.8 ppm on the basis of the anticipated isotope shift;[4] cf. the data in Table I).

Under experimental conditions similar to ours, the DiEt arrangement has been reported to produce resonances at 37.0–37.7 and 38.4–39.1 ppm which are due to the DiEt-br and DiEt-α carbons, respectively.[3d,47b,56,57b,65] Further examination of spectrum A, with reference to the discussion just given, reveals no convincing evidence for either signal, although a very weak DiEt-br peak could perhaps be escaping detection underneath the Me-α absorption. The absence of a significant DiEt-*d*-α resonance from spectrum B can be inferred from an argument analogous to the one that was used above in order to exclude the EtHe-*d*-α' peak. Lastly, we note that the Et-CH_3 resonance of spectrum A shows no clear indications of the broadening or multiplicity that the presence of EtHe and DiEt structures would have been likely to cause.[1d,56,66]

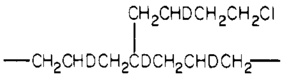
In short, there currently seems to be a complete lack of evidence for the existence of chlorinated 2-ethyl-*n*-hexyl and 1,3-diethyl branch groupings in the PVC specimen under study.

Partially Reduced Branch Structures. Kinetic arguments based on relative reactivity data have led us to anticipate the presence of significant amounts of *nonallylic primary halogen* in PVC samples whose reduction by Bu_3SnH (or Bu_3SnD) is nearly 100% complete.[3m,31] When the reductant is Bu_3SnH, this type of residual halogen could appear in ClBu, ClEt, and ClMe branch structures, whereas the use of Bu_3SnD could cause the residual halogen to occur in the corresponding ClBu-*d*, ClEt-*d*, and ClMe-*d* arrays. Indeed, we have obtained conclusive ^{13}C NMR evidence for the existence of ClBu and ClMe moieties in various Bu_3SnH-reduced PVC specimens (including sample A of the present study),[3m,31] and we have identified the ClBu-*d* and ClMe-*d* structures in our sample



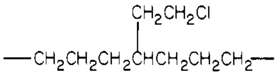
$-CH_2CH_2CH_2\overset{CH_2CH_2CH_2CH_2Cl}{C}HCH_2CH_2CH_2-$

ClBu



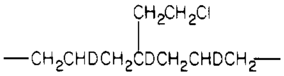
$-CH_2CHDCH_2\overset{CH_2CHDCH_2CH_2Cl}{C}DCH_2CHDCH_2-$

ClBu-*d*



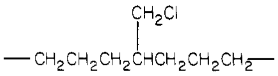
$-CH_2CH_2CH_2\overset{CH_2CH_2Cl}{C}HCH_2CH_2CH_2-$

ClEt



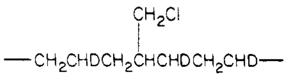
$-CH_2CHDCH_2\overset{CH_2CH_2Cl}{C}DCH_2CHDCH_2-$

ClEt-*d*



$-CH_2CH_2CH_2\overset{CH_2Cl}{C}HCH_2CH_2CH_2-$

ClMe



$-CH_2CHDCH_2\overset{CH_2Cl}{C}HCHDCH_2CHD-$

ClMe-*d*

Table II
Concentrations of the Branch Structures in Reductively Dehalogenated PVC

reduced polymer	polym temp, °C	reducing agent	frequency (±0.1) per 1000 C[a]					
			LB	Bu	ClBu	Et	Me	ClMe
A[b]	100	Bu_3SnH	0.3	0.9	0.3	0.8	2.0	0.3
B[b]	100	Bu_3SnD	0.4[c]	0.8[c]	0.3[d]	0.7[c]	2.2[c]	0.3[e]
S-54	75	Bu_3SnH	≤0.3	1.0	0.0	0.6	2.8	0.0
		$LiAlH_4$	≤0.3	0.9	≤0.3[f]	≤0.3	2.8	≤0.3[f]
E-54	75	$LiAlH_4$	≤0.3	≤0.5	≤0.5[f]	≤0.3	2.2	≤0.5[f]
R-23	56	$LiAlH_4$	≤0.2	≤0.2	≤0.3[f]	≤0.1	2.1	≤0.2[f]
S-80	43	Bu_3SnH	≤0.2	0.7	≤0.3	0.3	2.2	0.4
		$LiAlH_4$	≤0.2	≤0.3	≤0.3[f]	≤0.2	1.9	≤0.3[f]
E-80	43	$LiAlH_4$	≤0.3	≤0.6	≤0.4[f]	≤0.5	2.0	≤0.2[f]
103EP	*g*	Bu_3SnH	≤0.2	0.6	≤0.2	0.3	2.6	0.3

[a] Spectra obtained in earlier studies[2a–d,3g,l,m] were used to determine the values given here for the following polymers: S-54, E-54, R-23, S-80, and E-80. Branch concentrations reported elsewhere for these polymers[1a,b,2a–d,3g] and for samples A and B[1a,b,d,3g] have now been recalculated. Values preceded by ≤ refer to structures whose presence is uncertain. See Figure 3 and the text for nomenclature and discussion. [b] Spectrum shown in Figure 1. [c] Concentration of the corresponding deuterated structure in Figure 3. [d] ClBu-*d* concentration. [e] ClMe-*d* concentration. [f] Structure not expected to occur in $LiAlH_4$-reduced samples. [g] Value not available.

B.[31] Owing to a lack of suitable ^{13}C NMR reference data, ClEt and ClEt-*d* groups have not been found in reduced PVC thus far, but our kinetic analysis[3m,31] strongly suggests that these structures will eventually be detected in some of our reduced specimens. Furthermore, as discussed below, nonallylic primary halogen can also remain at the saturated long-chain ends of samples that have been reduced extensively.

In a forthcoming publication,[31] we will present complete details of our identification of the residual primary-halogen-containing structures in reductively dehalogenated PVC. Some of these details have been described in a preliminary communication.[3m]

Branch Concentrations. Table II contains concentration data, obtained by ^{13}C NMR, for all of the branch structures identified thus far in polymers A and B and in several other samples of reduced PVC that were polymerized under various conditions. Branch concentrations reported elsewhere for a number of these specimens[1a,b,d,2a–d,3g] have now been revised in order to accommodate the presence of Bu or Bu-*d* carbon signals. Observations similar to those described above for polymers A and B have given no evidence for the existence of Pr, Am, EtHe, or DiEt structures in the other reduced polymers of Table II.

It is important to note that the concentrations of the partially reduced branch structures do not change perceptibly upon going from sample A to sample B. For this reason, the presence of such structures does not invalidate the structural arguments, presented above, that are based upon signal strength comparisons between spectra A and B.

For all of the samples studied except polymers A and B, comparisons of the Bu-br + LB-br and Bu-α + LB-α peak intensities did not provide conclusive evidence for the presence of LB groups. Nevertheless, in view of the possible errors in the intensity measurements, these samples could have contained the LB structure at the levels indicated in Table II. Significantly, in the spectrum of polymer 103EP, which was recorded at 90.52 MHz, the unexpanded Bu-br + LB-br peak was noticeably asymmetric, as expected for a composite signal. For all of the polymers listed that were reduced with Bu_3SnH, it would obviously be of interest to examine the expanded Bu-br + LB-br resonance at a high magnetic field.

Most (or all) of the Bu resonances were observed in the ^{13}C spectra of the Bu_3SnH-reduced samples of Table II. These spectra also displayed the Et-α resonance and, usually, the Et-br signal, as well. Owing to its overlap with the Cl-γ resonance (at ~26.7 ppm)[2a,b,5b] or to its obscuration by base line drift, the Et-α' peak could not be assigned unambiguously in the spectra of the Bu_3SnH-reduced S-54, S-80, and 103EP materials. The same spectra failed to reveal an Et-CH_3 signal, but this result is not surprising in view of the long T_1[47] and low concentrations of the Et-CH_3 carbon.

Another significant feature of the data in Table II is the lack of conclusive spectral evidence for the presence of Bu and Et structures in most of the $LiAlH_4$-reduced polymer samples (note, however, that the Bu moiety was identified in the $LiAlH_4$-reduced polymer, S-54). In contrast, the Me structure appears at or near its expected concentration in most of the $LiAlH_4$-reduced specimens.[67] These results suggest that the chlorinated *n*-butyl and ethyl branch groupings have a strong predilection for side reaction during reductions with $LiAlH_4$, and that tertiary halogen must be present in order for the side reaction to occur. The nature of this reaction is uncertain, but branch-point dehydrochlorination may be involved, as there is some IR evidence for the occurrence of that process during the $LiAlH_4$ reduction of poly(vinyl chloride-*co*-2-chloropropenes)[30b] and PVC itself.[68] That the PVC–$LiAlH_4$ reaction can be capricious has been noted in previous papers.[2a–d]

Table II also shows that the (Bu + ClBu):Et ratio increases when the polymerization temperature is lowered. This observation indicates that the activation energy for reaction 3 is less than that for reaction 4, a result which is certainly not unreasonable in view of the different sizes of the transient rings that intervene in these rearrangements.[9e,58] The activation energy difference can be estimated roughly from our data, but it would be preferable to derive it instead from branch concentrations that are known more accurately and which also include some reliable values for the hypothetical ClEt segment. Nevertheless, it is clear already that PVC specimens prepared at low temperatures will contain relatively low concentrations of the 2-chloroethyl branch group. This temperature effect may account, at least partially, for the failure of other workers[3f,j,k] to identify the Et structure in some samples of Bu_3SnH-reduced PVC. Indeed, in a collaborative study with Dr. G. S. Park,[5d,31] we have found that the 2-chloroethyl branch concentrations are too low to be determined accurately for a series of PVC samples prepared in solution at 40 °C.

Since reactions 3 and 4 compete directly with normal chain propagation (i.e., with reaction 7), it is also possible,

$$2 + CH_2{=}CHCl \rightarrow -(CH_2CHCl)_3CH_2\dot{C}HCl \quad (7)$$

in principle, to estimate the following activation energy differences from the branch concentration results: $E_3 - E_7$ and $E_4 - E_7$. However, this type of calculation is complicated severely by various factors that relate to the determination of the average monomer concentration (which must be introduced, of course, in order to obtain the relative rate of reaction 7). In the case of bulk (or suspension) polymerization, for example, the vinyl chloride concentration in the monomer-swollen polymer phase will vary with the temperature.[38b,c,39e] This concentration will change with conversion, as well, after a certain conversion level has been reached,[39a-c,e,69] and the relative amounts of propagation occurring in the different phases of the system may also be determined by the temperature[39f,69] and the conversion.[39a-f,69] The quantitative aspects of all of these factors are controversial, and there is, in our opinion, insufficient information available now to allow their accurate numerical description over the temperature range of interest to us. Thus any attempts to determine the $E_3 - E_7$ and $E_4 - E_7$ values seem unwarranted at this time.

Effect of Tertiary Halogen on the Thermal Stability of PVC. Berens[28e] has compared the thermal stabilities (dehydrochlorination rates) of a number of ordinary PVC specimens with those of several poly(vinyl chloride-*co*-2-chloropropenes) whose tertiary halogen contents could be estimated from their extents of comonomer incorporation. This exercise showed that the instabilities of the PVC's themselves could be accounted for by the presence of only about 0.1–0.2 mol % [(0.5–1.0)/(1000 C)] of tertiary chloride sites, a range of values which is comparable to the sums of the Bu and Et concentrations that are reported in Table II for our Bu_3SnH-reduced PVC samples that had been polymerized at commercial temperatures. Moreover, it is important to note, for the purpose of specific comparison, that one of our polymers (S-80) had been synthesized at a temperature and conversion level (90%)[49c] which are about the same as those used for the preparation of one of the Berens PVC's (50 °C, 91% conversion).[28e] These findings strongly suggest that tertiary halogen is an important contributor to the thermal instability of the ordinary vinyl chloride homopolymer.

On the other hand, in some studies with PVC samples that had been prepared under monomer-starved conditions (U-PVC),[70] Sörvik and Hjertberg concluded that long-chain ends were the principal source of thermal instability,[70b,c] and that the destabilizing effect of long-branch points was relatively minor, at most.[70b,c] These findings would argue against destabilization by tertiary chloride if tertiary chloride were present at the long-branch points of the samples examined. However, later work has shown that U polymers probably contain appreciable amounts of internal unsaturation,[3f] as well as *n*-butyl-branch-bearing segments that, presumably, are tertiary-halogen sites.[3f,j,k] The relative contributions of these structures to the U polymer instability are problematical, but a significant contribution by tertiary chloride is now considered to be reasonable.[3j,k]

In the case of ordinary PVC, chloroallylic long-chain ends have been conclusively shown to be present[2e,10] (see below), and other unsaturated groups may occur as well, though in very small amounts.[1b,10] All of the unsaturated structures should be unstable,[1b] but there still remains to be resolved the question of whether their total effects on the polymer stability are as great as that of tertiary chloride.

Long-Chain Ends and the Mechanism of Chain Transfer to Monomer. Most of the long-chain ends in ordinary PVC are formed by chain transfer to the monomer,[39e,69,71] and this situation undoubtedly obtains for our 100 °C PVC specimen. As is to be expected when such a situation applies,[39e,69,71b] the $\bar{M}_w/\bar{M}_n$ ratio of this specimen is very close to 2; ratios of 2.1 and 1.9 can be calculated for reduced samples A and B, respectively, from data in the Experimental Section of this paper. Also, as anticipated,[69,71b,72] these data indicate a number-average degree of polymerization (200 for sample A; 230 for sample B) which is in excellent agreement with the $1/C_M$ values that can be obtained from the equations recommended for use by Kuchanov and Bort[69] or by Carenza et al.[72] ($1/C_M$ = 200[69] or 230,[72] where C_M is the monomer transfer constant).

Although the mechanism of transfer to monomer had been the subject of much discussion and speculation,[48a,71a,73] it had never actually been defined until recently. However, in 1979 we reported the details of some ^{13}C NMR measurements that provided strong evidence for the operation of a transfer process that could be regarded formally as proceeding via reactions 8–10,[4c,d] and at that time we announced that other structural evidence for such a mechanism had been obtained in our laboratory.[4c,d] This evidence showed conclusively that structure **10** was the principal saturated long-chain end in the polymer, a result that was presented orally in April, 1979, at the ACS/CSJ Joint Chemical Congress (Honolulu, HI)[4d] and published later in preliminary form.[1d] We now describe the details of our structural findings that have established the mechanism of eq 8–10 beyond all reasonable doubt.

$$-CHCl\dot{C}H- \rightarrow -CH{=}CH- + Cl\cdot \quad (8)$$

$$Cl\cdot + CH_2{=}CHCl \rightarrow ClCH_2\dot{C}HCl \quad (9)$$

$$ClCH_2\dot{C}HCl + CH_2{=}CHCl \rightarrow \xrightarrow{\text{etc.}} \underset{\mathbf{10}}{-CHClCH_2CHClCH_2Cl} \quad (10)$$

Spectrum A of Figure 1 and partial spectrum IV of Figure 2 contain resonances whose chemical shifts and relative intensities require their attribution to the LE long-chain end of Figure 3. The LE-CH_3 assignment is discussed above in the "2,4-Dichloro-*n*-butyl Branches" section, which also describes good evidence for the presence of an LE-4 carbon signal in the 50.31-MHz trace of spectrum A. In the 25.16-MHz trace of this spectrum, the LE-2 and LE-3 absorptions are easily detected, and the chemical shifts (Table I) of all of the LE resonances are in good agreement with the values obtained for appropriate reference substances,[31,54] including the copolymer mixture of Figure 4.

Spectrum B of Figure 1 shows that the LE ends of sample A are derived from *two* precursory structures containing halogen and that these structures correspond to the LE-*d* and LE-*d'* arrangements of Figure 3. The 50.31-MHz version of spectrum B contains a partially resolved 1:1:1 triplet signal which is upfield from the Bu-*d*-CH_2D triplet by ca. 0.10 ppm and has the predicted spacing[2e,4] of ~19 Hz. The isotope shift of this triplet (Table I) is consistent[2e,4] with its assignment to the LE-*d*-CH_2D and LE-*d'*-CH_2D carbon atoms (cf. spectra IV and V of Figure 2). In the 22–23-ppm region of spectrum B, there is strong evidence for the presence of two types of carbon that are contained in saturated long-chain ends. One type appears to be of the LE-*d*-2 variety, since it produces a singlet whose isotope shift (Table I) is indicative of the attachment of deuterium to each of the neighboring carbons.[4] The other type is the one that is designated as LE-*d*′-2; two components of its triplet signal ($J_{CD} \sim 19$ Hz) appear separately in spectrum B, and the coincidence of the third (downfield) component with the Bu-*d*-γ′ resonance can be inferred from the enhanced intensity of that resonance, which was pointed out in an earlier section. Additional strong support for the LE-*d*′-2 assignment is provided by the isotope shift (Table I).[4] Lastly, the 32-ppm region of spectrum B contains a singlet whose chemical shift compels its assignment to the LE-*d*′-3 carbon. It is important to realize that the isotope shift of this resonance (Table I) requires the presence of *two* deuterium neighbors[4] and that its corrected intensity (see below) is much greater than that of the LE-*d*-2 singlet. These observations conclusively rule out the possibility that the resonances designated as LE-*d*-2 and LE-*d*′-3 are actually produced by neighboring carbons that occur in a single structure. The LE-*d*-3 triplet is too weak for detection, as expected, and the absorptions of the principal carbons obscure the region of spectrum B where the LE-*d*-4 and LE-*d*′-4 resonances should appear. However, the presence of the deuterated LE-*d*′-4 carbon is established by the LE-*d*′-3 isotope shift; and the occurrence of the nondeuterated LE-*d*-4 carbon seems eminently reasonable, since the only apparent precursor for the rest of the LE-*d* structure is the long-chain end that would result from hydrogen abstraction by the growing-chain radical, **2**.

In order to determine accurately the long-chain-end concentrations, a 25.16-MHz spectrum of sample B was recorded with a pulse interval of 30.0 s (previous studies with polyethylene had shown that such a spectrum would yield quantitative results for the long-chain ends[34]). Most regions of this spectrum were satisfactory, but unfortunately, owing to poor resolution and base line drift, the spectrum was unsuitable for reliable measurement of the LE-*d*′-3 intensity. Nevertheless, the discussion that follows will show that the desired concentration values were derivable from this spectrum and the information already on hand.

For sample A, the true LE-3/LE-2 resonance intensity ratio should obviously be 1.0. Yet in the 50.31-MHz spectrum of this sample, which was obtained at a pulse interval of 5.0 s, the LE-3/LE-2 intensity ratio is actually 1.2. The 50.31-MHz spectrum of sample B was also recorded with a 5.0-s pulse interval; thus the LE-*d*′-3/LE-*d*-2 intensity ratio determined from this spectrum should also be greater than its true value by a factor of ~1.2. Application of this correction leads to a true LE-*d*′-3/LE-*d*-2 intensity ratio of 3.3, a value that should represent the true LE-*d*′/LE-*d* concentration ratio as well. From the relative intensity of the LE-*d*-2 resonance in the 30.0-s pulse spectrum of sample B, the true LE-*d* concentration is calculated to be 0.5/(1000 C). Multiplication of this value by 3.3 then yields a true value of 1.7/(1000 C) for the LE-*d*′ concentration. Spectrum B also contains a resonance at ca. 44.6 ppm that undoubtedly arises from the CH_2Cl carbons of three structures whose reduction is incomplete.[3m,31] These structures are the ClBu-*d* arrangement shown above and the ClLE-*d* and ClLE-*d*′ long-chain

$$\underset{\text{ClLE-}d}{-CH_2CHDCH_2CH_2Cl} \qquad \underset{\text{ClLE-}d'}{-CHDCH_2CHDCH_2Cl}$$

ends.[3m,31] From other resonances in spectrum B,[3m,31] the ClBu-*d* concentration can be estimated to be ca. 0.3/(1000 C), and the ClLE-*d*′/ClLE-*d* and LE-*d*′/LE-*d* ratios can be assumed to be about the same. In the spectrum recorded with a 30.0-s pulse interval, the intensity of the 44.6-ppm resonance corresponds to a total carbon concentration of 0.9/(1000 C); hence the ClLE-*d*′ and ClLE-*d* concentrations appear to be about 0.5 and 0.1/(1000 C), respectively. Summing in order to obtain the total concentrations of the saturated long-chain ends in the unreduced polymer, we find that LE-*d*′ + ClLE-*d*′ = **10** = (2.2 ± 0.4)/(1000 C) and LE-*d* + ClLE-*d* = **11** = (0.6 ± 0.2)/(1000 C) (the deviations are estimated values).

$$\underset{\mathbf{11}}{-CH_2CHClCH_2CH_2Cl}$$

Within the likely limits of error, the concentration of **11** is equivalent to the number of long-branch points in sample B. This finding supports the mechanism suggested above for long-branch-point formation. Further, if essentially all of the long-chain ends except **11** are indeed formed via reactions 8–10, one **10** end should be present per number-average PVC molecule. From the $\bar{M}_n$ determined for sample B by gel permeation chromatography (GPC), the concentration of **10** in the starting polymer is predicted to be about 2.2/(1000 C). Thus the GPC and NMR results for **10** conform completely, and the transfer process of eq 8–10 can now be regarded as well established.

Our data provide no indications for the operation of any competing mechanism for transfer to the monomer, and there is, in particular, no evidence for the mechanism of eq 11 and 12, whose possible occurrence has been considered seriously in some recent publications.[48a,73b,c] Such a mechanism is extremely unlikely a priori, since H· β scission (eq 11) is relatively unfavorable energetically (for simple gaseous alkyl radicals, its activation energy is ca. 40 kcal/mol),[74] and it apparently has never been detected experimentally in any system for which there exists the possibility of a competing Cl· β scission (eq 8; gas-phase activation energies for such reactions are only about 20 kcal/mol[45]). Moreover, there is no experimental evidence for the formation of either of the chain-end structures that would result from the addition, to vinyl chloride, of an actual or incipient hydrogen atom. These structures are the $-CHClCH_2CHClCH_3$ arrangement and the less likely chain end $-CHClCH_2CH_2CH_2Cl$, derived from a $ClCH_2\dot{C}H_2$ adduct radical.

$$-CHCl\dot{C}H- \rightarrow -CCl{=}CH- + H\cdot \qquad (11)$$

$$H\cdot + CH_2{=}CHCl \xrightarrow{\text{etc.}} \text{polymeric radical} \qquad (12)$$

In theory, several specific polymer radicals could undergo reaction 8. One possibility, considered independently by other workers,[27b,75] is a radical (**5**) that is formed by hydrogen abstraction (eq 13). However, for the following reasons, **5** is unlikely to be a major source of the chlorine atoms that are transferred to the monomer: (1) For sample B, the number of internal double bonds, plus the number of 1,2-di(long alkyl)cyclopentanes derived from these groups upon reduction,[10] is much less than the number of **10** ends in the original PVC specimen. (2) The growing-chain radical, **2**, obviously is the only carbon radical whose steady-state concentration will be high enough to allow it to serve as R′· in eq 13 to any appreciable extent. For a mechanism involving eq 13 (R′· = **2**), followed by eq 8–10, the number of **11** ends (R′H in eq 13) must be at least as large as the number of **10** ends in the polymer. This condition clearly is not fulfilled. Nevertheless, within the error limits of our measurements, the **11** concentration could be slightly higher than the concentration of long-branch points. Hence we cannot rule out the possibility that the mechanism now being considered does operate in a minor way.

$$-CHClCH_2CHCl- + R'\cdot \rightarrow \mathbf{5} + R'H \qquad (13)$$

Much more likely candidates for involvement in reaction 8 are the long-chain head-to-head radical, **12**,[4c,d] and the radical, **13**, that results from its rearrangement[4c,d] (eq 14). The β scission of these species would produce the chain end **6** (eq 15 and 16) and/or its allylic isomer, **14** (eq 17),

$$\underset{\mathbf{12}}{\mathrm{-CH_2CHClCHCl\dot{C}H_2}} \rightarrow \underset{\mathbf{13}}{\mathrm{-CH_2CHCl\dot{C}HCH_2Cl}} \tag{14}$$

$$\mathbf{12} \rightarrow \mathbf{6} + \mathrm{Cl\cdot} \tag{15}$$

$$\mathbf{13} \rightarrow \mathbf{6} + \mathrm{Cl\cdot} \tag{16}$$

$$\mathbf{13} \rightarrow \underset{\mathbf{14}}{\mathrm{-CH_2CH{=}CHCH_2Cl}} + \mathrm{Cl\cdot} \tag{17}$$

and conclusive evidence has, in fact, been obtained for the existence of one or both of these chain ends in our 100 °C PVC. This evidence has been provided by the complete 50.31-MHz ^{13}C NMR spectra of reduced samples A and B, which have established the presence of 1-ethyl-2-(long alkyl)cyclopentane chain ends that could only have been created by the reduction of **14** and/or **6**.[2e,10] Quantitative NMR measurements of the cyclopentane concentrations have shown that **14** and/or **6** must have comprised *at least* ~70% of the unsaturated long-chain ends of the unreduced polymer (assuming one unsaturated end per number-average molecule),[2e] and our NMR spectra have given no indications for the existence of any other unsaturated ends.[2e] Questions that now remain to be considered are the relative importance of eq 15–17 and whether the labile chlorine atom actually exists as Cl· or is simply transferred directly via a one-step reaction of the monomer with **13** and/or **12**. These problems will be discussed in full in a later publication,[31] but it seems worth noting here that, at this writing, all of the available evidence appears consistent with either of the following alternatives: (a) reversible occurrence of reaction 17, followed by a rate-determining addition of Cl· to vinyl chloride; (b) direct reaction of **13** with vinyl chloride to produce **14** and the $\mathrm{ClCH_2\dot{C}HCl}$ radical.

Several other workers have attempted to identify the long-chain ends in PVC using NMR techniques. In a ^{1}H NMR study of a number of PVC specimens, Caraculacu and Bezdadea obtained results for unsaturated structures that were ambiguous[76] and thus provided no conclusive evidence for the presence of either **14** or **6**. Another ^{1}H NMR investigation was reported by Pêtiaud and Pham,[77] who observed some resonances that were thought to derive from **14** and a chain end, $\mathrm{-CH_2CH_2CHClCH_2Cl}$, resulting from the reaction of **14** with HCl that was formed in situ. No signals attributable to **11** were found,[77] the formation of chain ends by transfer to monomer was not discussed, and the molecular-weight dependencies of the intensities of the supposed chain-end resonances[77] were entirely inconsistent with the monomer transfer mechanism that has been established in the present work. Observations similar to those of Pêtiaud and Pham have been made by other researchers,[3f,78] and the interpretive uncertainty of the ^{1}H NMR approach has been affirmed.[78a]

Schwenk et al.[79] have used ^{1}H and ^{13}C NMR methods to examine a very low molecular weight fraction of PVC (0.07% of the total polymer) that had been isolated by methanol extraction. The spectra were obtained both before and after the fraction had been subjected to catalytic hydrogenation, and the results were said to indicate the presence of the chain ends **15** and **16**, at concentrations of 0.5 and 0.25 per polymer molecule, respectively, together with **17** and **18**, whose total concentration was stated to be 1.25 per molecule, with **17** being the more abundant of these two structures (the exact **17**:**18** ratio was not determined).[79] End group **15** was plausibly suggested to have resulted from the methanolysis of structure **14** (although methanolysis of **6** with rearrangement was considered as a possible alternative), while **17** and **18** were considered to be contained in structures **10** and **11**, whose presence was not actually established.[79] In order to account for the formation of **14** and **10**, the authors proposed a mechanism which includes eq 18, 17, 9, and 10 (in that order), whereas the production of **11** and **16** was rationalized in terms of eq 19–22.[79]

$$\underset{\mathbf{15}}{\mathrm{-CHClCH_2CH{=}CHCH_2OCH_3}}$$

$$\underset{\mathbf{16}}{\mathrm{-CH_2CHClCH{=}CHCH_2Cl}}$$

$$\underset{\mathbf{17}}{\mathrm{-CHClCH_2Cl}} \qquad \underset{\mathbf{18}}{\mathrm{-CH_2CH_2Cl}}$$

$$\mathbf{2} \rightarrow \mathbf{13} \tag{18}$$

$$\mathrm{H\cdot + CH_2{=}CHCl \rightarrow ClCH_2\dot{C}H_2} \tag{19}$$

$$\mathrm{ClCH_2\dot{C}H_2} + n\mathrm{CH_2{=}CHCl} \rightarrow \underbrace{\mathrm{ClCH_2CH_2CHClCH_2}}_{\mathbf{11}}\mathrm{(CHClCH_2)_{\mathit{n}-2}CH_2\dot{C}HCl} \tag{20}$$

$$\mathrm{-CH_2CHClCH_2CH_2\dot{C}HCl \rightarrow -CH_2CHClCH_2\dot{C}HCH_2Cl} \tag{21}$$

$$\mathrm{-CH_2CHClCH_2\dot{C}HCH_2Cl} \rightarrow \mathbf{16} + \mathrm{H\cdot} \tag{22}$$

We believe that several of these suggestions are open to serious question. In the first place, reactions 18 and 21 are most improbable, for reasons discussed elsewhere,[4c] and the former process has, in fact, been excluded convincingly by some of our previous work.[4c,d] Secondly, H-atom β scission (eq 22) is very unlikely, for the reasons given above, and the addition of H· to vinyl chloride would be expected to yield the $\mathrm{CH_3\dot{C}HCl}$ radical preferentially, as this radical is likely to be more stable, thermodynamically, than the radical product of reaction 19.[4c] Yet there is no evidence from our studies or those of others[3k,22,77,79] for the presence of the $\mathrm{-CHClCH_2CHClCH_3}$ chain ends that would result from the addition of $\mathrm{CH_3\dot{C}HCl}$ to monomer. Thirdly, repetitive tail-to-head propagation (eq 20) is, to our knowledge, entirely without precedent in the case of vinyl chloride. Cyclohexyl radicals, for example, are known to experience preferred addition to the $\mathrm{CH_2}$ end of this monomer,[80] and by analogy with the behavior of other 2-chloroalkyl radicals (including radical **12**),[4c,d] the propagating $\mathrm{-CHClCH_2CHCl\dot{C}H_2}$ radical of eq 20 would certainly undergo a very rapid 1,2 Cl migration that should preclude its addition to the monomer to any major extent. Finally, it is not clear why the methanolysis of **16** would not occur under the conditions that apparently yielded structure **15**.[79] In view of the lack of evidence for this methanolysis,[79] the extreme improbability of reactions 19–22, and our failure to find **16**,[2e] we recommend a reevaluation of the spectral data[79] that were thought to support the occurrence of that structure.

On the apparent assumption that these data[79] are equally consistent with the presence of chain end **19**, Caraculacu[27b] has proposed a mechanism for **19** formation that involves eq 23 and 24. This scheme must also be regarded as highly unlikely in view of the considerations noted above.

$$\mathbf{12} + \mathrm{CH_2{=}CHCl} \rightarrow \mathrm{-CH_2CHClCHClCH_2CH_2\dot{C}HCl} \quad (23)$$

$$\mathrm{-CH_2CHClCHClCH_2CH_2\dot{C}HCl} \rightarrow \underset{\mathbf{19}}{\mathrm{-CH_2CHClCHClCH{=}CHCH_2Cl}} + \mathrm{H\cdot} \quad (24)$$

Other Mechanistic and Structural Implications. There currently appears to be no reason for believing that other important commercial monomers can undergo a monomer transfer process like that established here for vinyl chloride. Thus the operation of this mechanism probably accounts for the well-known observation that the C_M of vinyl chloride is much greater than the C_M's of other common monomer types.[71a,81]

During vinyl chloride polymerization, the chain-transfer constants of trichloroethylene[82] and *trans*-1,2-dichloroethylene[71a,83] are even greater than that of the monomer itself. This finding strongly suggests that the transfer mechanisms for trichloroethylene and *trans*-1,2-dichloroethylene are similar to that for vinyl chloride, since the addition of growing-chain radicals to the double bonds of these transfer agents would invariably generate species that could undergo chlorine-atom β scission. With both agents, the transfer process is indeed accompanied by some copolymerization,[82,83] and in the case of trichloroethylene, this type of mechanism is implicated further by the near identity of the transfer constants found for trichloroethylene-*h* and trichloroethylene-*d* in homogeneous solution polymerizations.[82] (Under heterogeneous conditions, trichloroethylene-*d* gave an isotope effect for chain transfer of approximately 1.75,[82] but the observation of this rather small value can perhaps be ascribed to the difficulties involved in applying the Mayo equation to heterogeneous systems.) In the case of the isomeric 1,2-dichloroethylenes, another argument for the operation of a chlorine-atom transfer process has been presented by Dawson et al.[73a]

Finally, we note that the presence of the truncated "head-to-head" structure, **10**, can account for some of the published evidence for the existence of backbone head-to-head linkages in PVC. Head-to-tail propagation proceeding from radical **12** would generate the backbone structure, **20**, whose ^{13}C chemical shifts have been reported

$$\underset{\mathbf{20}}{\mathrm{-CH_2CHClCHClCH_2CH_2CHCl-}}$$

by Keller and Mügge.[84] With recourse to these shift values,[84] we have been unable to obtain any NMR evidence for the presence of **20** in a number of unreduced PVC samples, including a ^{13}C-enriched specimen (prepared in bulk at 60 °C) for which the detection limit of **20** was estimated to be about 0.5/(1000 C).[34] Nevertheless, using iodometric titration as the method of analysis, Mitani et al.[85] have found head-to-head linkage concentrations ranging from ca. 1.3 to 3.8/(1000 C) in several PVC samples that had been polymerized at various temperatures. The order of magnitude of these concentrations is the same as that expected for the concentrations of **10** in this sample series if the presence of one **10** end per polymer molecule is assumed. Moreover, since the extent of transfer to monomer increases as the polymerization temperature is raised,[69,72] the occurrence of **10** accounts qualitatively for the reported effect of temperature[85] on the iodometric head-to-head values. On the other hand, the quantitative agreement of these values[85] with our estimated **10** concentrations leaves something to be desired. Attempts to find **20** in PVC are continuing in these laboratories.

Note Added in Proof. We have just obtained a copy of a recent doctoral dissertation (Hjertberg, T., Chalmers University of Technology, Sweden, 1982) that describes the ^{13}C NMR analysis of several samples of $\mathrm{Bu_3SnH}$- and $\mathrm{Bu_3SnD}$-reduced PVC. The author's results provide additional support for many of the structural and mechanistic conclusions that had already been established in our earlier papers and have now been collated above.

Experimental Section

Materials. Vinyl chloride (Matheson) was passed through a column of 3A molecular sieves, condensed at −78 °C, subjected to several cycles of freeze–pump–thaw degassing in order to remove dissolved oxygen, and then distilled at 10^{-6} torr. The middle fraction was retained for use; its analysis by gas chromatography–mass spectrometry (GC–MS) revealed no 2,4-dichloro-1-butene or other impurities, at a probable detection limit of ca. 0.02 wt % [this analysis was performed with a Varian MAT-112 instrument using TIC detection, helium as carrier gas, a 10 ft × 0.125 in. (o.d.) column packed with 10% of OV-101 on 100–120 mesh Chromosorb W, and a temperature programming range of 25–150 °C]. The PVC samples designated as S-54, E-54, R-23, S-80, and E-80 have been described elsewhere in the literature.[30c,49c] Commercial PVC (Geon 103EP, BFGoodrich), ethylene–1-octene copolymer (5571-2, Du Pont), ethylene–1-hexene copolymer (Marlex J316, Phillips), and ethylene–1-butene copolymer (HPD 5502, Arco) were used without purification. Branch concentrations of the copolymers, as determined by ^{13}C NMR, were *n*-hexyl = 2.6/(1000 C), Bu = 12.8/(1000 C), and Et = 4.7/(1000 C), respectively.[34] Tri-*n*-butyltin hydride (Ventron) and tri-*n*-butyltin deuteride (Ventron) also were used as received; IR analysis showed that the latter reagent was deuterated to the extent of at least 99%. Tetrahydrofuran (THF, Mallinckrodt) and 2-methyltetrahydrofuran (MTHF, Aldrich) were distilled at reduced pressure and passed under nitrogen through a column of activated alumina immediately prior to use. Toluene (Matheson Coleman and Bell reagent grade) and xylene (Matheson Coleman and Bell reagent grade, mixture of isomers, nominal bp 137–144 °C) were dried over 5A molecular sieves. The other chemicals were highly purified commercial materials requiring no further treatment.

Preparation of PVC in Bulk at 100 °C. In a typical experiment, a mixture of vinyl chloride (5.02 g) and 1,1′-azobis(cyclohexanecarbonitrile) (1.4 mg) was prepared in a thick-walled Pyrex ampule and frozen in liquid nitrogen. The ampule was then sealed under high vacuum, heated in an oil bath for 4.0 h at 100.0 ± 0.1 °C, and opened at liquid-nitrogen temperature. Unchanged monomer was removed by distillation under high vacuum, and the monomer conversion was calculated from the weight of the residual polymer (conversions of 54 and 57% were obtained in two sets of simultaneous quadruplicate runs). The polymer was recovered by filtration after slurrying in methanol and purified by dissolution in a 1:1 (v/v) mixture of acetone and carbon disulfide, followed by precipitation with excess methanol and drying in vacuo for several hours at 45 °C. GC–MS analysis (see above) of the recovered monomer fractions showed that they did not contain 2,4-dichloro-1-butene.

Reductive Dehalogenation of PVC. The 100 °C bulk polymer was reduced with $\mathrm{Bu_3SnH}$ or $\mathrm{Bu_3SnD}$ in two stages, according to the general procedure employed previously for reductions with $\mathrm{Bu_3SnH}$.[2a,b] The first stage of the $\mathrm{Bu_3SnH}$ reduction was carried out under nitrogen using 3.75 g of the polymer, 20.63 g of $\mathrm{Bu_3SnH}$ [1.18 mol/(mol of monomer units)], and 90 mg of azobis(isobutyronitrile) (AIBN) in 320 mL of refluxing MTHF. This reaction afforded 1.58 g of polymeric product, which was subjected to a further reduction in xylene (210 mL) under nitrogen at 88–96 °C using 3.37 g of the organotin hydride and 40 mg of AIBN. Purification of the reduced polymer (1.38 g) by treatment with HCl in xylene,[2a,b] followed by precipitation with methanol, Soxhlet extraction with methanol, and drying in vacuo at ca. 50 °C, gave 1.17 g of the material whose ^{13}C NMR spectrum is presented in Figure 1A. Analysis of this polymer by gel permeation chromatography indicated the following molecular weights (as compared to linear polyethylene standards): $\bar{M}_n$ = 5600, $\bar{M}_w$ = 11 900.

The initial stage of the $\mathrm{Bu_3SnD}$ reduction was performed under argon in refluxing THF (275 mL) using 5.00 g of polymer, 40.0 g of $\mathrm{Bu_3SnD}$ [1.71 mol/(mol of monomer units)], and 120 mg of

AIBN. Further reduction of the polymer (2.15 g) was effected in xylene (250 mL) under argon at 86–95 °C with 9.1 g of Bu_3SnD and 60 mg of AIBN. The reduced polymer was purified by Soxhlet extraction into xylene under nitrogen through an Alundum thimble of 0.1-μm porosity,[2d] followed by precipitation with methanol, Soxhlet extraction with methanol (two extraction–precipitation–extraction sequences were performed), and drying in the usual way. These operations yielded 1.67 g of the product whose ^{13}C NMR spectrum is displayed in Figure 1B. Analysis of this material by gel permeation chromatography gave $\bar{M}_n$ = 6600 and $\bar{M}_w$ = 12 400 (vs. linear polyethylene standards).

Geon 103EP, polymer S-54, and polymer S-80 were reduced with Bu_3SnH in the customary manner,[2a,b] except for omission of the second stage of reduction in the case of the latter polymer (^{13}C NMR analysis showed that the one-stage reduction of this material was 99.7% complete[2c,d]).

The $LiAlH_4$ reductions were performed according to a procedure that has been described elsewhere in detail.[86] This procedure involves the use of ca. 1.25 mol of the reducing agent per mol of vinyl chloride monomer units in THF solution under nitrogen at 100 °C.[86]

Preparation of 1-*n*-Octylcyclohexanecarbonitrile. The method used is similar to that of Tilford et al.[87] All synthetic operations were carried out under nitrogen.

Cyclohexanecarbonitrile (10.95 g, 0.100 mol) was added dropwise with stirring during 0.7 h to a solution of sodium amide (4.50 g, 0.115 mol) in liquid ammonia (ca. 60 mL) at –75 to –65 °C. Stirring was continued while a solution of 1-bromo-*n*-octane (22.21 g, 0.115 mol) in anhydrous toluene (50 mL) was introduced dropwise during 0.4 h at –65 to –58 °C. The mixture was allowed to warm gradually to 10 °C while standing overnight. It was then diluted with anhydrous toluene (50 mL), refluxed with stirring for 2.7 h, and filtered under vacuum. The spearated solid was washed on the filter with several portions of dry toluene, and the combined filtrate and washings were fractionated under vacuum through an 80-plate spinning-band column to obtain 19.13 g (yield, 86%) of 1-*n*-octylcyclohexanecarbonitrile: bp 119–124 °C (5 torr) [lit.[87a] bp 163–166 °C (16.0 torr; product evidently was impure[87a])]; IR (neat) 2240 cm^{-1} (strong, CN); mass spectrum, m/e 221 (weak, M^+); ^{13}C NMR (25.16 MHz, 1,2,4-trichlorobenzene, 110 °C) δ 14.11, 22.91, 23.49, 24.76, 26.02, 29.53, 29.73, 30.21, 32.18, 36.30, 39.26, 40.98, and 122.98 ppm vs. Me_4Si (see main text for assignments of resonances that are pertinent to the present work). Anal. Calcd for $C_{15}H_{27}N$: C, 81.38; H, 12.29; N, 6.33. Found: C, 81.09; H, 12.13; N, 6.86.[88]

Attempted Reaction of Vinyl Chloride with HCl. Vinyl chloride (5 mL) and anhydrous HCl (0.2 mL) were condensed in a thick-walled Pyrex ampule at −80 °C (the volumes were measured at this temperature), and the ampule was then sealed under high vacuum and heated at 100 ± 0.1 °C for 3.5 h. Analysis of the mixture by GC–MS (see above for experimental details) gave no evidence for the formation of 2,4-dichloro-1-butene or other organic products.

^{13}C NMR Measurements. The 25.16-MHz spectra of the reduced 100 °C polymers were obtained with a Varian XL-100 instrument that was modified for pulse Fourier transform spectroscopy and interfaced with a Nicolet Model 1080 computer. Protons were decoupled from the carbon nuclei using a random noise decoupling field. The pulse angle was 90°; free induction decays were stored in 8K computer locations using a spectral window of 5000 Hz (i.e., a dwell time of 100 μs). Hexamethyldisiloxane was used as an internal reference (2.0 ppm vs. Me_4Si), and the internal deuterium lock signal was provided by p-dioxane-d_8. Samples were observed at 110 °C as solutions in 1,2,4-trichlorobenzene; polymer concentrations were 15% (w/v) (spectrum A, Figure 1) or 32% (w/v) (spectrum B, Figure 1). Spectrum A represents an accumulation of 47 750 transients at a pulse repetition time of 5.0 s; spectrum B represents 10 800 scans at a pulse repetition time of 6.0 s. Under the conditions employed, T_1 is ca. 1.3 s for the principal CH_2 carbons of reduced, nondeuterated PVC.

The spectra of the reduced S-54, E-54, R-23, S-80, and E-80 polymers also were recorded at 25.16 MHz, using previously described procedures[2c,d] that are very similar to those employed for polymers A and B. The spectrum of the reduced Geon 103EP polymer was obtained in an analogous way at 90.52 MHz on a Bruker HX-360 instrument with 32K data points, a sweep width of 9091 Hz, and a total accumulation of 17 830 transients at a pulse repetition time of 3.0 s.

Spectra were recorded at 50.31 MHz using a Varian XL-200 instrument with 32K data points, a sweep width of 8000 Hz, and a procedure which was identical otherwise, in all important respects, with that used in order to obtain the 25.16-MHz spectra of polymers A and B. The following information pertains to the various 50.31-MHz spectral runs (sample, sample concentration, pulse repetition time, number of transients): A and B, 20% (w/v), 5.0 s, 14 000; mixture of ethylene–1-hexene and ethylene–1-butene copolymers, 20% (w/v), 4.0 s, 16 615; mixture of ethylene–1-octene and ethylene–1-hexene copolymers, 10% (w/v), 3.0 s, 18 000. At 50.31 MHz under our experimental conditions, the principal CH_2 carbons of these polymers have a T_1 of approximately 1.8 s.

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Registry No. PVC, 9002-86-2; vinyl chloride, 75-01-4.

References and Notes

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