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Detailed Microstructure and Concentration of the Chlorinated n-Butyl Branches in Poly(vinyl chloride)

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SUMMARY

The ^{13}C NMR spectra of reductively dehalogenated samples of poly(vinyl chloride) (PVC) have provided conclusive evidence for the presence of 2,4-dichloro-n-butyl branches in the original polymer. These branches are contained in a

$-CHCl-CH_2-CCl(CH_2-CHCl-CH_2-CH_2Cl)-CH_2-CHCl-$

arrangement which is formed as the result of a radical "backbiting" reaction. For a series of polymers prepared in conventional ways at temperatures of 43 to 100 °C, the 2,4-dichloro-n-butyl branch concentration ranges from about 0.6 to 1.0/(1000 C).

Introduction

Recent studies in these laboratories have shown that the ^{13}C NMR spectra of reductively dehalogenated PVC samples can provide remarkable amounts of information about the molecular structures of the original polymers. These studies have been reviewed (STARNES, JR. in press). Although PVC has been reduced with $LiAlH_4$ and $LiAlD_4$, Bu_3SnH and Bu_3SnD are now the reductants of choice (STARNES, JR. et al. 1978, STARNES, JR. et al. 1979a). When a deuterated reagent is used, each chlorine atom of the polymer is replaced by an atom of deuterium. As a consequence, the proton-decoupled NMR signals of the resultant deuterated carbons appear as triplets rather than singlets, and these signals, as well as those of adjacent carbons, experience significant upfield shifts. Thus, by comparing the ^{13}C NMR spectra of hydride- and deuteride-reduced polymer specimens, one can determine both the carbon skeleton and the chlorine substitution pattern of the original material. This approach has already given strong indications for the occurrence of n-butyl branches in reduced samples of PVC (STARNES, JR. et al. 1980a, STARNES, JR. in press), and the presence of such branches has been supported by several investigations involving the use of other analytical techniques (STARNES, JR. in press). However, the chlorine substitution pattern of the n-butyl branch arrangement has not been reported thus far. We now wish to summarize briefly the results of

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additional experiments which have allowed us to deduce the entire microstructure and the concentration of the chlorinated n-butyl branches in PVC.

Results and Discussion

PVC was prepared by free-radical polymerization in bulk at 100 °C. Aliquot portions of the polymer were reduced with Bu_3SnH or Bu_3SnD (STARNES, JR. et al. 1978) in order to obtain the specimens whose ^{13}C NMR spectra are presented in Figure 1 (where the B:A signal intensity ratio is roughly 2:1). Sample A appears to have been reduced completely, as the downfield portions (not shown) of its 25.16- and 50.31-MHz spectra contain no resonance near 63.7 ppm which can be assigned to the chloromethylene carbon of a $-CH_2-CH_2-CHCl-CH_2-CH_2-$ backbone structure (STARNES, JR. et al. 1978). In contrast, the spectra of sample B exhibit a weak "Cl-d-α" carbon signal at 63.70 ppm which, as ex-

$$\text{-CHD-}\overset{\beta}{\text{CH}_2}\text{-}\overset{\alpha}{\text{CHCl}}\text{-}\overset{\beta}{\text{CH}_2}\text{-CHD-} \qquad \text{-}\overset{\beta}{\text{CH}_2}\text{-}\overset{\alpha}{\text{CH}_2}\text{-CO-}\overset{\alpha}{\text{CH}_2}\text{-}\overset{\beta}{\text{CH}_2}\text{-}$$

Cl-d　　　　　　　　CO

pected, is about half as intense as the probable "Cl-d-β" resonance at 39.03 ppm (ABBAS et al. 1975). Nevertheless, these two resonances indicate the presence of only ca. 0.05 mol % of residual halogen.

Both reduced specimens give a weak resonance near 32.8 ppm which has been tentatively assigned to CH_2 carbons that are α to internal trans double bonds ["DB-α" and "DB-d-α" assignments; cf. BOVEY et al. (1975) and STARNES, JR. et al. (1978)]. Sample A also affords resonances at 42.87 ppm (not shown) and 24.31 ppm which can be assigned, respectively, on the basis of comparative data for oxidized polyethylene (SCHILLING unpublished), to the α and β carbons of a "CO" backbone structure formed by adventitious autoxidation. The low-gain trace of spectrum B consists of a singlet and an overlapping triplet whose spectral characteristics are entirely consistent with expectations for poly(CH_2CHD) (BOVEY et al. 1975, STARNES, JR. et al. 1979b), and it is very important to note in this connection that spectrum B contains no evidence whatsoever for scrambling of the deuterium label.

In keeping with earlier observations (BOVEY et al. 1975), the spectra of Figure 1 provide conclusive evidence for the presence of chloromethyl branches [ca. 2.1/(1000 C)] in the starting polymer. These branches appear as an "Me" structure in spectrum A and an "Me-d" structure in spectrum B. The spectra also reveal the presence of 2-chloroethyl branches (STARNES, JR. et al. 1980a) [appearing as "Et" or "Et-d" structures; ca. 0.8/(1000 C)] and two types of saturated long-chain end resulting from chain-transfer processes (STARNES, JR. et al. 1980a) (these ends appear as an "LE" structure or as "LE-d" and "LE-d'" arrays). The resonances of the reduced samples that are associated with these groupings will be considered later in detail (STARNES, JR. et al. manuscript in preparation).

For purposes of direct comparison with the spectra

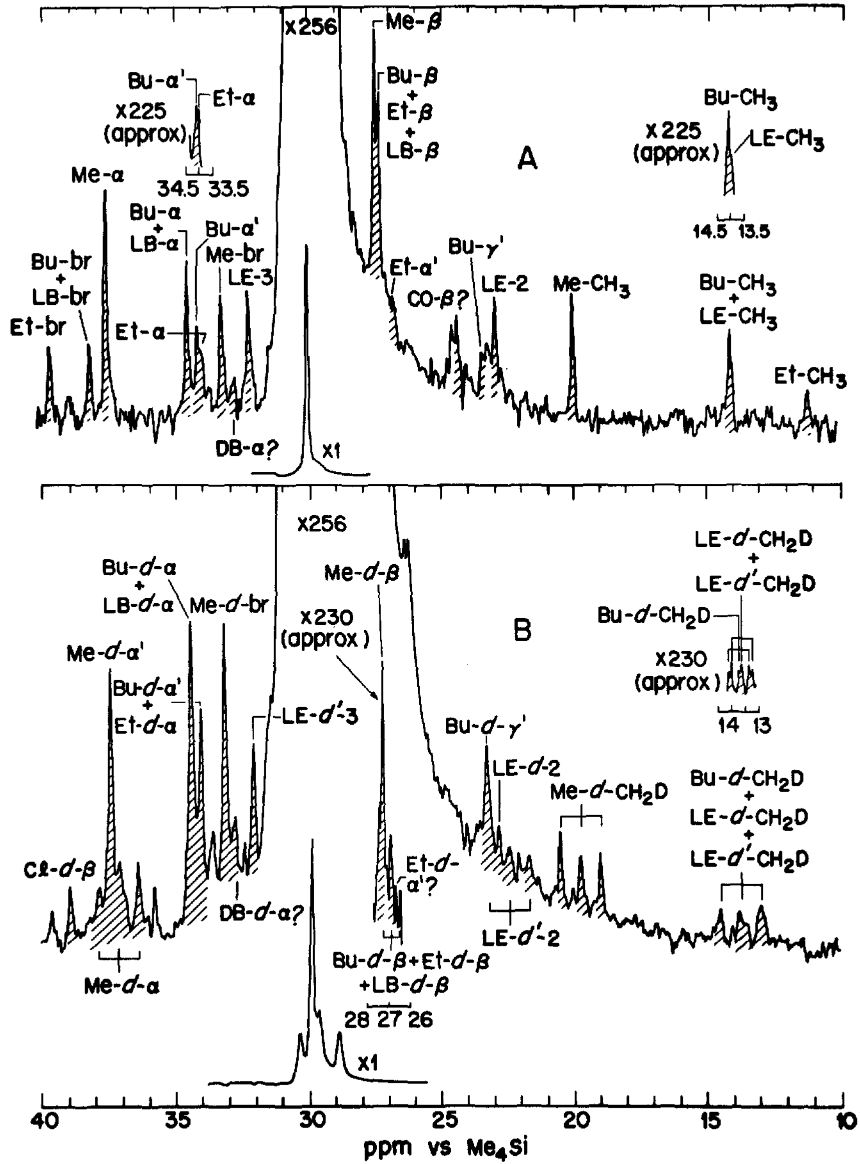
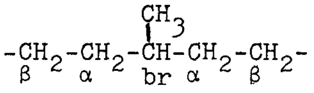
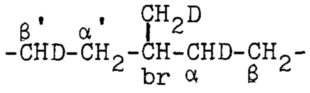


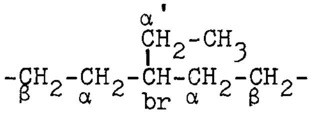
Figure 1. Proton-decoupled ^{13}C NMR spectra of PVC reduced with: A, Bu$_3$SnH; B, Bu$_3$SnD. Traces designated as "X1" and "X256" were obtained at 25.16 MHz; partial spectra shown as insets were recorded at 50.31 MHz.



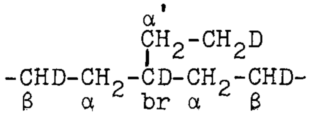
Me



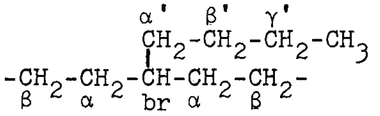
Me-d



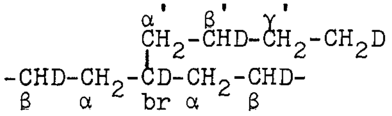
Et



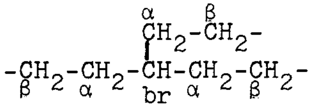
Et-d



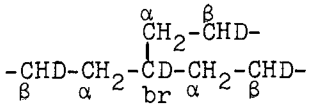
Bu



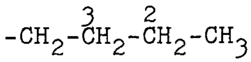
Bu-d



LB

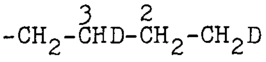


LB-d



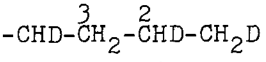
$-CH_2-\overset{3}{C}H_2-\overset{2}{C}H_2-CH_3$

LE



$-CH_2-\overset{3}{C}HD-\overset{2}{C}H_2-CH_2D$

LE-d



$-CHD-\overset{3}{C}H_2-\overset{2}{C}HD-CH_2D$

LE-d'

of Figure 1, we have obtained the 50.31-MHz spectrum of a mixture of ethylene-(1-butene) and ethylene-(1-hexene) copolymers containing known amounts of ethyl and n-butyl branches, respectively. This spectrum is displayed in Figure 2, which contains peak assignments that are based on those of RANDALL (1973) and on the relative peak intensities. Noteworthy aspects of the copolymer mixture spectrum are the clear-cut separation of the "Bu-α'" and "Et-α" resonances and the appearance of the "LE-CH_3" resonance as an upfield shoulder on the "Bu-CH_3" peak (these features can be seen more easily in a full-size spectral trace). The "LE-CH_3" and "Bu-CH_3" assignments are further confirmed by some 50.31-MHz ^{13}C spectral data that have been obtained for other samples of reduced PVC having different "Bu":"LE" ratios (STARNES, JR. et al. to be published).

On the basis of the information contained in the spectra of Figures 1 and 2, we are now able to state unequivocally that 2,4-dichloro-n-butyl branch structures are present in the PVC sample of the current study. Upon reduction, these structures are converted into "Bu" or "Bu-d" groups whose carbons have the chemical shifts that are recorded in Table I. The tabulated shifts of the "Bu" carbons are in good agreement with the values reported by RANDALL (1973) and with the "Bu" shifts obtained independently from the spectrum of Figure 2. The "Bu-CH_3" and "Bu-α'" signals are clearly distinguishable in the 50.31-MHz insets of spectrum A, while the "Bu-γ'" resonance appears in the 25.16-MHz tracing. Separate signals are not observed in spectrum A for the "Bu-br", "Bu-α", and "Bu-β" carbons, owing to the presence of overlapping resonances arising from the "Et-β" carbons and the carbons of a long-branch point ("LB") (RANDALL 1973, BOVEY et al. 1976). Nevertheless, when the relative intensities of

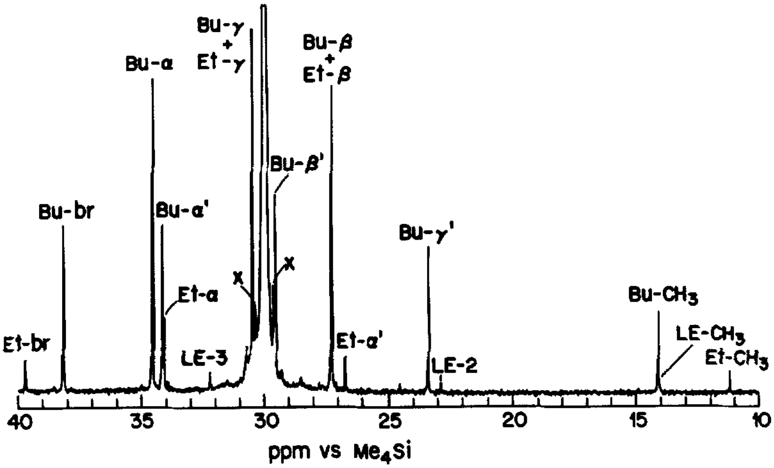


Figure 2. Proton-decoupled ^{13}C NMR spectrum (50.31 MHz) of a 2:1 ethylene-(1-hexene):ethylene-(1-butene) copolymer mixture. Signals denoted by "X" are spinning side bands on the principal CH_2 resonance.

TABLE I

^{13}C Shifts of "Bu" and "Bu-d" Carbons in Reduced PVC

Carbon	δ,[a] ppm vs. Me_4Si		Isotope Shift, ppm vs. Me_4Si	Isotope Substitution Pattern
	Bu_3SnH-reduced	Bu_3SnD-reduced		
Bu-br	38.18	---	---	---
Bu-α	34.51	---	---	---
Bu-β	27.22	---	---	---
Bu-α'	34.15	---	---	---
Bu-γ'	23.35	---	---	---
Bu-CH_3	14.07	---	---	---
Bu-d-α	---	34.38	-0.13	2 neighbors
Bu-d-β	---	26.89[b]	-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[b]	-0.28	1 attached

[a] Estimated accuracy, ±0.05 ppm. [b] Triplet center.

the resonances at 38.18 and 34.51 ppm are compared, it becomes obvious that the "Bu-br" and "Bu-α" signals are the major contributors to these two peaks (see below).

In spectrum B, the "Bu-*d*-CH$_2$D" carbon appears as a triplet which is partially resolved at 50.31 MHz and has the anticipated spacing of ca. 19 Hz (BOVEY et al. 1975, STARNES, JR. et al. 1979b). However, the "Bu-*d*-γ'" resonance remains as a singlet whose relative intensity is found to be identical to that of the "Bu-γ'" resonance of spectrum A when a correction is made for the presence of an underlying branch of the "LE-*d*'-2" triplet. The ("Bu-*d*-br" + "LB-*d*-br") signal cannot be detected, but this result is certainly not inconsistent with the presence of branch carbons bearing deuterium (STARNES, JR. et al. 1979b). Since the "Bu-*d*-β", "Et-*d*-β", and "LB-*d*-β" carbons would be deuterated also, their composite resonance should appear as a triplet. Two components of this triplet (J_{CD} ~ 20 Hz) can, in fact, be identified in the 50.31-MHz trace. The non-deuterated "Bu-*d*-α" and "LB-*d*-α" carbons yield a composite singlet, as expected, but only one singlet appears in the spectral region where the "Bu-*d*-α'" and "Et-*d*-α" carbons should absorb (even at 50.31 MHz, the resonances of these carbons are not resolved). Owing to the presence of a drifting baseline, accurate intensity measurements cannot be made from the 25.16-MHz trace of spectrum B in the (34-35)-ppm region. However, the baseline drift is negligible in this portion (not shown) of the 50.31-MHz scan. Comparisons made between the latter tracing and the 50.31-MHz trace of spectrum A show that the ("Bu-*d*-α" + "LB-*d*-α") and ("Bu-α" + "LB-α") resonances have identical relative intensities, and that the relative intensity of the resonance denoted as ("Bu-*d*-α'" + "Et-*d*-α") is equal to the sum of the relative intensities of the "Bu-α'" and "Et-α" signals. These results constitute conclusive evidence for the presence of the "Bu-*d*-α" and "Bu-*d*-α'" carbons in sample B. Finally, we note that the isotope shifts (Table I) of all of the identified "Bu-*d*" resonances are in accord with the values expected on the basis of previous work (BOVEY et al. 1975, STARNES, JR. et al. 1979b).

In view of the ^{13}C NMR results that have been reported for the relevant poly(ethylene-*co*-1-alkene)s (RANDALL 1973, BOVEY et al. 1976), it has been obvious to us for some time that the presence of *n*-butyl branches in reductively dehalogenated PVC would affect the "LB" concentration determined from the resonances near 34.5 and 38.2 ppm. Appropriate T_1 measurements (SCHILLING unpublished) have shown that the intensities of these resonances can be compared quantitatively under the conditions used to obtain spectrum A. From such a comparison, we estimate a "Bu" concentration of ca. 0.9/(1000 C) and an "LB" concentration of ca. 0.3/(1000 C) for the polymer under study. The "Bu" value is in good agreement [$\pm$0.1/(1000 C)] with the values derived from the "Bu-α'" and "Bu-γ'" resonances [when T_1 differences (SCHILLING unpublished) are taken into account], and the presence of the "LB" arrangement in other reduced samples of PVC has been supported by the appearance of a downfield shoulder on the ("Bu-br" + "LB-br") peak after scale expansion (STARNES, JR. et al. to be published).

The chlorinated n-butyl branches are undoubtedly formed via a "backbiting" reaction (BOVEY and TIERS 1962) of the ordinary growing-chain radical, -CH_2-CHCl-CH_2-$\dot{C}$HCl. This conclusion is strongly reinforced by our discovery, adumbrated orally (STARNES, JR. 1980b) but not yet published, that PVC samples obtained by homogeneous solution polymerization show increasing concentrations of these branches with decreasing concentrations of vinyl chloride (STARNES, JR. et al. to be published).

Encouraged by the findings described above, we have reexamined the ^{13}C spectra of several Bu_3SnH-reduced PVC's that were polymerized under "commercial" conditions at temperatures of 43 to 75 °C (STARNES, JR. et al. 1979a, STARNES, JR. in press) and have found that these polymers all contain "Bu" groups in concentrations ranging from ca. 0.6 to 1.0/(1000 C). At such levels, the tertiary Cl of chlorinated "Bu" structures would be expected to contribute significantly to the thermal instability of PVC (BERENS 1974).

To our knowledge, other investigators have reported no conclusive NMR evidence for the presence of n-butyl branches in reduced samples of ordinary poly(vinyl chloride). However, in an interesting study by HJERTBERG and SÖRVIK (1980), "Bu" groups apparently were detected in a reduced PVC that had been prepared under monomer-starved conditions [although the "Bu-CH_3" assignment of HJERTBERG and SÖRVIK (1980) does not agree with ours]. HJERTBERG and SÖRVIK (1980) did not determine the chlorine substitution pattern of the n-butyl branches, and the "Bu" and "LB" concentrations cannot be derived convincingly from their published spectrum, owing to differences among the peak heights of some of the "Bu" carbon resonances that are inconsistent with expectations based on the "Bu" carbon T_1's (AXELSON et al. 1977, SCHILLING unpublished).

Experimental

The PVC was prepared in bulk at 100.0$\pm$0.1 °C using 1,1'-azobis(cyclohexanecarbonitrile) as a thermal radical source. Ethylene-(1-hexene) copolymer (Marlex J316, Phillips) and ethylene-(1-butene) copolymer (HPD 5502, Arco) contained "Bu" and "Et" concentrations of 12.8 and 4.7/(1000 C), respectively, as determined by ^{13}C NMR. Reductions of PVC were performed according to procedures resembling the one that was previously discussed (STARNES, JR. et al. 1978, STARNES, JR. et al. 1979a). Pulse Fourier transform ^{13}C NMR spectra were obtained at 25.16 MHz with a Varian XL-100 spectrometer that was interfaced with a Nicolet Model 1080 computer, and at 50.31 MHz with a Varian XL-200 instrument, using a technique similar to that described in earlier publications [e. g., see STARNES, JR. et al. (1979a)]. The following information pertains to the various spectral runs (sample, field strength, sample concentration in 1,2,4-trichlorobenzene, pulse repetition time, number of transients): A, 25.16 MHz, 15% w/v, 5.0 s, 47 750; A, 50.31 MHz, 20% w/v, 5.0 s, 14 000; B, 25.16 MHz, 32% w/v, 6.0 s, 10 800; B, 50.31 MHz, 20% w/v, 5.0 s, 14 000; copolymer mixture, 50.31 MHz, 20% w/v, 4.0 s, 16 615.

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