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# Ethylene–Vinyl Bromide Copolymers by Reductive Debromination of Poly(vinyl bromide). A Carbon-13 NMR Study

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ABSTRACT: We have prepared a series of ethylene–vinyl bromide copolymers (0–100 mol % vinyl bromide) by reductive debromination of poly(vinyl bromide) with tributyltin hydride. The compositional and stereosequence microstructures have been determined by $^{13}$C NMR. Removal of bromine is a random process with respect to compositional sequence, and meso stereosequence dyads are slightly more reactive than racemic dyads. Minor structural irregularities have been assigned in PVB after its complete reduction to polyethylene. The major chain defect (ca. 1%) is a hydroxyl branch caused by $S_N2$ displacement of bromine in the presence of water. The chain end groups are an olefin and a *cis*-1-methyl-2-alkylcyclopentyl group. Some internal cyclopentyl groups are observed also. The concentration of *n*-alkyl branches is negligible in the reduced material owing to steric inhibition of head-to-head monomer addition and chain-radical back-biting steps during vinyl bromide polymerization.

Recently, we characterized the stereosequence microstructure of poly(vinyl bromide) (PVB)[1] and its model compounds[2] by $^{13}$C NMR. Other microstructural features of interest in the PVB chain include end groups, branches, unsaturation, and possible head-to-head linkages. In view of the success of $^{13}$C NMR in examining analogous details in poly(vinyl chloride) (PVC) after complete reductive dehalogenation by organometallic hydrides,[3] we have adopted this approach in the present work.

Alternatively, if PVB is incompletely reduced, a material equivalent to an ethylene–vinyl bromide (E–V) copolymer is obtained. To our knowledge this material has not been synthesized by the direct copolymerization of ethylene with vinyl bromide. Its study by $^{13}$C NMR would provide useful data on bromine substituent effects[4] in spectra of polymers and allow a statistical analysis of the course of the reduction of PVB to be made if the distribution of reacted units could be ascertained.

In this paper we analyze 50.3-MHz $^{13}$C NMR spectra of PVB's at stages of reduction varying from 0 to 100% debromination. The above aspects of polymer microstructure are considered and compared with results from published studies on PVC.

## Experimental Section

**Materials.** Commercial PVB (Polysciences, Inc.; prepared at 50 °C in aqueous suspension with lauroyl peroxide) and PVB prepared in our laboratory[1] were used as starting materials. The commercial sample was dissolved in carbon disulfide–acetone, precipitated in cold methanol, and vacuum-dried at room temperature overnight. Its molecular weight averages were $\bar{M}_n$ = 10 600 and $\bar{M}_w$ = 28 700 according to GPC analysis.

**Reductive Debrominations.** Reductions by tri-*n*-butyltin hydride (Alfa Products, Ventron Division) were carried out under a nitrogen atmosphere in tetrahydrofuran or 2-methyltetrahydrofuran that had been passed through basic alumina. Recrystallized azobis(isobutyronitrile) was used as the initiator at a concentration of about 1 mol % of polymer. Low levels of reduction were achieved overnight by a one-pass procedure at 50 °C with about 10% excess hydride over the amount calculated for the desired level of reduction. Complete reduction required a two-pass procedure with excess hydride and a second stage at 80 °C in 2-methyltetrahydrofuran.

**NMR Spectra.** $^1$H NMR spectra were obtained at 60 MHz on a Varian T-60 A spectrometer. Polymer solutions were prepared in 5-mm sample tubes at 5% by volume concentration in methylene-$d_2$ chloride or chloroform-$d$ and observed at ambient temperature.

A Varian XL-200 spectrometer was used to acquire $^{13}$C NMR data at a frequency of 50.3 MHz. Typically, 10 000 transients were accumulated from a 25% by volume polymer solution in a 10-mm sample tube, with a delay from 4.0 to 10.0 s (depending on sample $T_1$ values) between 90° pulses (14.0-μs duration). A sweep width of 8000 Hz was used with 32K computer locations (acquisition time 2.0 s).

The solvent was dictated by polymer composition. Samples with over 50% reduction were dissolved in either 1,2,4-trichlorobenzene or hexachlorobutadiene with sufficient perdeuteriobenzene or dioxane to maintain field lock and observed at 110 °C. Some samples with high bromine content dehydrobrominated at elevated temperatures and were therefore observed as solutions in either chloroform-$d$ or tetrahydrofuran-$d_8$ at 50 °C, where this problem was not as acute.

## Results and Discussion

**1. $^1$H NMR Spectra.** The $^1$H NMR spectra of PVB at various stages of reduction are shown in Figure 1. The methine or CHBr proton gives a broad, featureless resonance with a maximum that shifts gradually upfield from 4.6 to 4.0 ppm as the bromine content of the polymer decreases.

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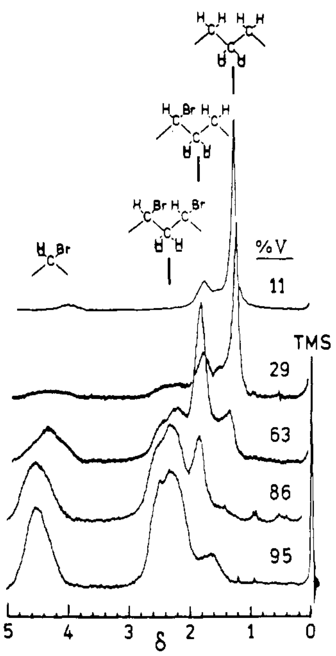


**Figure 1.** 60-MHz $^1$H NMR spectra of ethylene–vinyl bromide copolymers containing 95–11 mol % vinyl bromide. The observed protons are underlined. TMS = tetramethylsilane (0.00 ppm).

The methylene proton resonance is split into three peaks at 2.4, 1.8, and 1.2 ppm. These correspond to the three compositional sequence dyads VV, VE (EV), and EE, respectively, where V represents the vinyl bromide unit $CH_2CHBr$ and E represents the ethylene unit $CH_2CH_2$.

The composition of these polymers may be expressed as the mole percent of V units in an E–V copolymer. It may be calculated from the resonance areas in Figure 1 as follows. If $A(CHBr)$ is the total methine proton resonance area and $A(CH_2)$ is the total methylene proton resonance area, then $\% \mathrm{V} = 100\{4A(\mathrm{CHBr})/[2A(\mathrm{CHBr}) + A(\mathrm{CH_2})]\}$. The percent bromine removed during the course of the reduction, i.e., the extent of reaction of the original PVB, is simply 100 − % V.

The values calculated from the $^1$H NMR spectra in Figure 1 are in excellent agreement with independent figures calculated from analytical results for the weight percent of carbon, hydrogen, and bromine in the samples.

**2. $^{13}$C NMR Spectra.** The $^{13}$C NMR spectra of polymers containing 100, 63, and 0 mol % V are shown in Figure 2. These spectra reveal polymer microstructure in far greater detail than the $^1$H NMR spectra discussed above. The spectrum of the homopolymer PVB (100 mol % V) has been analyzed previously.[1,2] There are two basic types of resonance given by E–V copolymers: those due to methine or CHBr carbons (58–49 ppm) and those due to methylene or $CH_2$ carbons (49–25 ppm). These assignments were confirmed in off-resonance, proton-decoupled spectra and by measurements of spin–lattice relaxation times. The nearly threefold greater chemical shift dispersion of the methylene carbon resonances in comparison to the methine carbon resonances is a consequence of the greater magnitude of the shift effect of bromine as a $\beta$ substituent compared to a $\gamma$ substituent (ca. +10.6 vs. −2.0 ppm, respectively).[1,2,4]

Thus, there are three major groups of methylene carbon resonances around 47, 37, and 27 ppm, depending on whether the observed carbon has two, one, or no $\beta$-bromine substituents, respectively. The corresponding sequence environments are VV, VE (EV), and EE. Similarly, the methine carbon can have two, one, or no $\gamma$-bromine substituents in the respective sequences VVV, VVE (EVV), and EVE. The $\gamma$ effect is shielding, in contrast to the deshielding $\beta$ effect, so the VVV sequence gives the highest field resonance for the methine carbon but the lowest field resonance for the methylene carbon.

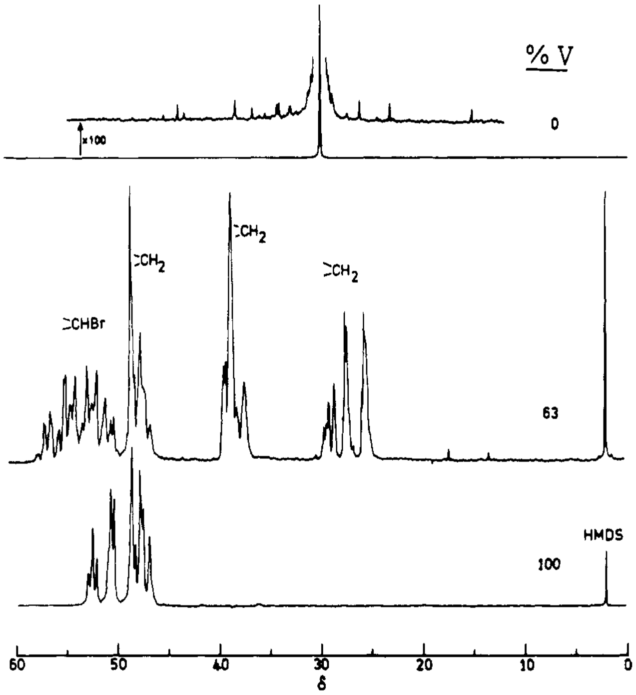


**Figure 2.** 50.3-MHz $^{13}$C NMR spectra of poly(vinyl bromide) (100% V, bottom trace), an ethylene–vinyl bromide copolymer with 63% V (middle trace), and polyethylene (0% V, top trace). HMDS = hexamethyldisiloxane (2.00 ppm).

The polymer obtained by 100% debromination of PVB is a polyethylene $(CH_2CH_2)_n$. Its spectrum (Figure 2) consists of a single, sharp line at 30.00 ppm. Some weak signals can be seen after suitable vertical amplification, and these are due to end groups, branches, and defects, which will be discussed after the sequence isomerism in E–V copolymers has been considered.

The dispersion of methine carbon resonances owing to stereoisomerism is not much less than their dispersion from monomer sequence isomerism, partly because of the small $\gamma$ effect of bromine. The CHBr resonances therefore suffer from considerable overlap, and they are not as amenable to analysis as the better separated $CH_2$ resonances.

**(a) Methylene Carbon Region.** Figure 3 shows the $CH_2$ resonance region (25–50 ppm) in detail. Representative assignments are indicated for monomer sequences and, where appropriate, stereoconfigurational sequences. In order to simplify the description of monomer sequences, we represent a $CH_2$ carbon by 0 and a CHBr carbon by 1. Thus, a VVE sequence is 010100, for example, and 1's must be separated by an odd number of 0's for a regular head-to-tail sequence of monomer units.

Monomer sequence assignments were deduced as follows. The largest influence on $CH_2$ chemical shift is from the $\beta$-bromine effect, which distinguishes three environments, 101, 100 (001), and 000, as described above. The 101 environment occurs to the exclusion of others in the homopolymer PVB, thereby establishing its basic chemical shift of 47 ppm. Since each $\beta$-bromine substituent causes a downfield shift of ca. 10 ppm, it follows that 100 (001) and 000 will be observed around 37 and 27 ppm, respectively.

The second significant influence is from the $\gamma$-bromine effect, which pertains to 000-centered sequences. Each $\gamma$-bromine substituent induces a shielding effect, so the

Table I
Methylene Carbon (0) Chemical Shifts Observed for Different Compositional Sequences in Ethylene-Vinyl Bromide Copolymers

| compositional sequence | % V | no. of Br substituents | | obsd δ ± 0.05 ppm | |
|---|---|---|---|---|---|
| | | β | γ | in $CDCl_3$ at 50 °C | in TCB[a] at 100 °C |
| 010 101 010 | 100 | 2 | 0 | 46.06–48.36 | 46.74–48.53 |
| 010 101 000 | 75 | 2 | 0 | 47.18, 48.26 | 47.68, 48.53 |
| 000 101 000 | 50 | 2 | 0 | 48.36 (m + r) | 48.78 (r), 48.58 (m) |
| 010 100 010 | 75 | 1 | 0 | 38.01 (r), 37.28 (m) | 38.81 (r), 37.51 (m) |
| 010 100 000 | 50 | 1 | 0 | 38.01 (r), 37.04 (m) | 38.64 (r), 37.36 (m) |
| 000 100 010 | 50 | 1 | 0 | 38.60 | 39.44 |
| 000 100 000 | 25 | 1 | 0 | 39.24 | 39.51 |
| 010 000 010 | 50 | 0 | 0 | 28.70 | 28.82 |
| 010 000 000 | 25 | 0 | 0 | 29.06 | 29.34 |
| 000 000 000 | 0 | 0 | 0 | 29.66 | 30.00 |
| 100 000 001 | 40 | 0 | 0 | 29.47 | 29.68 |
| 100 000 000 | 20 | 0 | 0 | 29.58 | 29.89 |
| 101 000 001 | 60 | 0 | 1 | 27.43 | 27.49 |
| 101 000 000 | 40 | 0 | 1 | 27.56 | 27.59 |
| 100 000 100 | 40 | 0 | 1 | 27.56 | 27.59 |
| 001 000 000 | 20 | 0 | 1 | 27.64 | 27.80 |
| 101 000 101 | 80 | 0 | 2 | 25.42–25.79 | 25.40–25.97 |
| 101 000 100 | 60 | 0 | 2 | 25.60–25.95 | 25.57–25.97 |
| 001 000 100 | 40 | 0 | 2 | 25.56, 25.71 | 25.70, 25.99 |

[a] TCB = 1,2,4-trichlorobenzene.

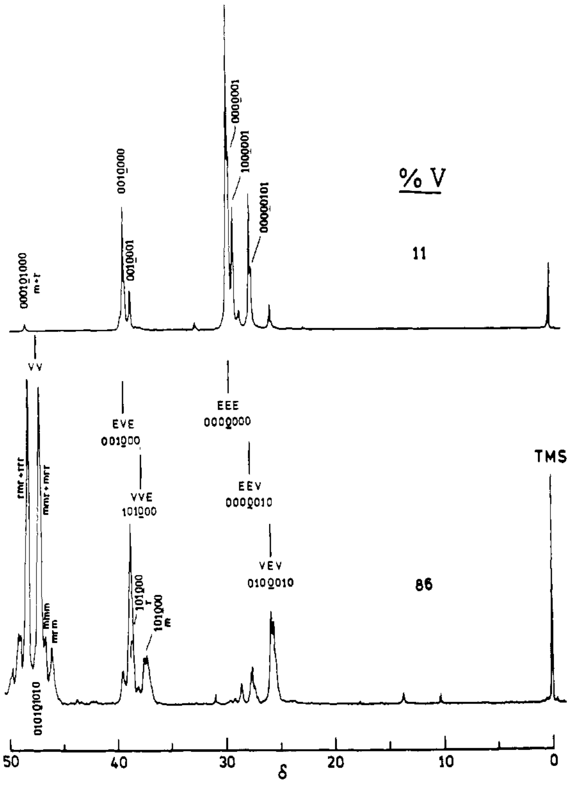


**Figure 3.** Expansion of the methylene carbon (0) resonances from ethylene–vinyl bromide copolymers with 86 and 11% V. The central (observed) methylene carbon is underlined in the binary compositional sequence designation.

sequences 00000, 10000 (00001), and 10001 will be ordered from low to high field with a spacing equal to this effect. Their respective chemical shifts show that $\bar{\gamma}_{CH_2,Br}$ has a value[2] of −2 ppm.

Stereoisomerism is the next important source of chemical shift nonequivalence. The central methylene carbon in the 1010101 sequence is dispersed over 3 ppm by tetrad stereoconfigurational sequences, which were assigned according to the PVB spectrum.[1,2] Our $^{13}C$ NMR results from the model compound 2,4,6-tribromoheptane showed that the chemical shift of a methylene carbon depends more on the stereochemical identity of its neighboring dyad than its surrounding dyad.[2] Thus, stereochemical splitting of the resonance from the central methylene carbon in the 000101000 sequence is barely resolved (0.2 ppm), given that the surrounding stereochemical dyad is both r and m (other regions of the spectrum confirm that both stereoisomers are present). However, we do observe a significant splitting (1.3 ppm) of the central methylene in the 1010000 sequence according to the relative stereochemistry of its neighboring dyad (r downfield from m).

The spectra are also sensitive to monomer sequence tetrads. Assignments at this level were made by considering the relative intensities of fine-structure multiplets as a function of copolymer composition; for example, as the % V content of the copolymer decreases, the probability of occurrence of sequences having longer runs of methylene carbons (0) must increase.

Detailed assignments of the methylene carbon resonances are given in Table I. Their chemical shifts are sensitive to solvent (and to a lesser extent temperature), and values are reported for deuteriochloroform and 1,2,4-trichlorobenzene solutions. Exact stereochemical assignments were not made for some compositional sequences, where the range of chemical shift is indicated instead.

**(b) Methine Carbon Region.** Figure 4 displays an expansion of the CHBr resonance region (49–59 ppm). The total dispersion of chemical shift (ca. 10 ppm) is only twice the spread induced by stereochemical nonequivalence in the homopolymer PVB. It is therefore difficult to separate the effects of compositional sequence and stereosequence on chemical shift within this region.

Some specific assignments can be made from model compound data[2] and by observing spectra from copolymers at both extremes of the composition range (e.g., 11 and 95% V), where the major peak intensity is concentrated in only a few compositional sequence types. An additional constraint on these peak assignments involves their areas,

Table II
Methine Carbon (1) Chemical Shifts Observed for Different Compositional Sequences in Ethylene-Vinyl Bromide Copolymers

| compositional sequence | % V | no. of γ-Br substituents | obsd δ ± 0.05 ppm in $CDCl_3$ at 50 °C | obsd δ ± 0.05 ppm in TCB[a] at 100 °C |
|---|---|---|---|---|
| 101 010 101 | 100 | 2 | 54.4-49.5[b] | 52.8-48.2 |
| 101 010 100 | 80 | 2 | 54.4-49.5 | 52.8-48.2 |
| 001 010 100 | 60 | 2 | 54.6 (rr), 52.5 (mr), 50.4 (mm) | 53.3 (rr), 51.1 (mr), 48.9 (mm) |
| 101 010 001 | 80 | 1 | 56.0-54.4 (r), 53.8-51.6 (m) | 55.7-54.1 (r), 53.5-51.4 (m) |
| 101 010 000 | 60 | 1 | 56.0-54.4 (r), 53.8-51.6 (m) | 55.7-54.1 (r), 53.5-51.4 (m) |
| 001 010 001 | 60 | 1 | 56.0-54.4 (r), 53.8-51.6 (m) | 55.7-54.1 (r), 53.5-51.4 (m) |
| 001 010 000 | 40 | 1 | 56.2 (r), 54.0 (m) | 55.8 (r), 53.7 (m) |
| 100 010 001 | 60 | 0 | 58.1 ($\hat{r}\hat{r}$),[c] 57.5 ($\hat{m}\hat{r}$), 56.9 ($\hat{m}\hat{m}$) | 57.5 ($\hat{r}\hat{r}$), 57.0 ($\hat{m}\hat{r}$), 56.5 ($\hat{m}\hat{m}$) |
| 100 010 000 | 40 | 0 | 58.2 ($\hat{r}$), 57.6 ($\hat{m}$) | 57.7 ($\hat{r}$), 57.2 ($\hat{m}$) |
| 000 010 000 | 20 | 0 | 58.45 | 57.86 |

[a] TCB = 1,2,4-trichlorobenzene. [b] Individual stereochemical assignments given in ref 1 and 2. [c] $\hat{r}$ = RS (SR) pair and $\hat{m}$ = RR (SS) pair of asymmetric centers separated by four backbone bonds.

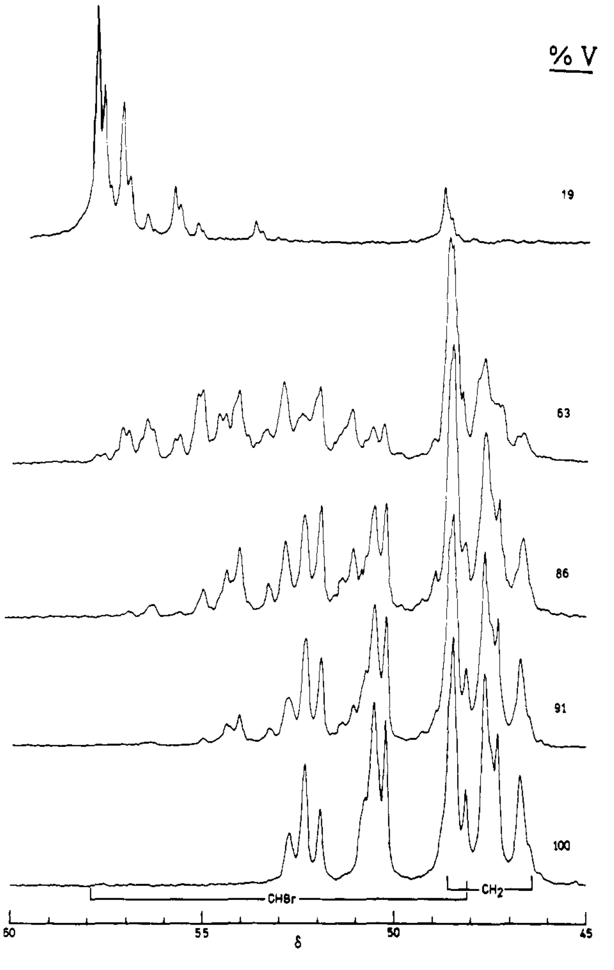


**Figure 4.** Expansion of the methine carbon resonances from ethylene-vinyl bromide copolymers with compositions ranging from 100 to 19% V. There is some overlap with methylene carbon resonances from 49 to 46 ppm.

which must be consistent with the areas for methylene carbon resonances already assigned (Table I) in corresponding sequences.

Table II shows the assignments deduced for the methine carbon resonances according to the foregoing rationale. The chemical shifts are sensitive to compositional and stereosequence pentads. Discrete stereochemical assignments could not be made for all of the ten nonequivalent compositional pentads, although the appropriate range of chemical shift has been ascertained.

**3. Sequence Distribution.** In this section we examine the compositional and stereosequence distribution in E–V copolymers as a function of the extent of reduction of the parent PVB. The methylene carbon resonances will be used predominantly for this purpose, owing to their greater sensitivity to structural nonequivalence compared to the methine carbon resonances.

Due consideration must be given to the dynamic aspects of the $^{13}C$ NMR experiments in order to assess the quantitative reliability of a sequence analysis based on resonance areas. These areas will give an exact measure of the proportions of different sequence environments, provided all carbon magnetizations are allowed to return to their equilibrium values between sampling pulses and the nuclear Overhauser enhancement factor $\eta$ is independent of sequence type. The former condition was met simply by choosing a pulse delay period of $5T_1(\max)$, where $T_1(\max)$ is the longest spin–lattice relaxation time encountered.

Our $T_1$ measurements showed, not unexpectedly, that segmental mobility or the local motional autocorrelation time $\tau_c$ as monitored by $T_1$ is a function of monomer sequence type. For example, in the copolymer with 63% V, the central methylene carbons in the sequence triads 101, 100, and 000 have $T_1$ values of 0.12, 0.15, and 0.28 s, respectively (measured at 35 °C in $CDCl_3$ at a magnetic field strength of 2.11 T). These values illustrate the damping effect bromine side groups exert on local motions; $\tau_c$ is longer ($T_1$ shorter) in sequences with higher bromine content.

We did not measure explicit $\eta$ values for various copolymer sequences. As will be seen from the subsequent analysis, however, there is no discrepancy to suggest that $\eta$ varied significantly for sequences within a given copolymer.

Compositional sequence dyad and triad probabilities are shown in Table III. Although some compositional tetrads and pentads were assigned (Tables I and II), these were not resolved sufficiently for accurate area measurements. The same difficulty prevented measurement of the probabilities of V-centered triads, which are given by the relative areas of methine carbon (1) resonances. The E-centered triad probabilities were derived from the set of resonances at 25–30 ppm, and the VV, VE, and EE dyad probabilities were obtained from the three principal resonance groups centered at 47, 37, and 27 ppm, respectively.

Table III
Comparison of Measured Unconditional Probabilities of Compositional Sequences in Ethylene-Vinyl Bromide Copolymers According to Analysis of Methylene Carbon Resonance Areas with Values Computed for a Bernoullian Distribution (Parentheses)

| | | probability | | | | | |
|---|---|---|---|---|---|---|---|
| | | dyads | | | E-centered triads | | |
| % V[a] | V | VV | VE | EE | VEV | VEE | EEE |
| 95 | 0.94 | 0.888 | 0.056 | 0.000 | 0.056 | 0.000 | 0.000 |
| | | (0.884) | (0.056) | (0.004) | (0.053) | (0.003) | (0.000) |
| 86 | 0.86 | 0.735 | 0.127 | 0.011 | 0.116 | 0.011 | 0.000 |
| | | (0.739) | (0.120) | (0.019) | (0.103) | (0.017) | (0.003) |
| 63 | 0.65 | 0.400 | 0.248 | 0.104 | 0.179 | 0.069 | 0.036 |
| | | (0.422) | (0.227) | (0.122) | (0.148) | (0.079) | (0.043) |
| 19 | 0.14 | 0.014 | 0.123 | 0.740 | 0.020 | 0.103 | 0.637 |
| | | (0.019) | (0.120) | (0.740) | (0.017) | (0.103) | (0.636) |

[a] According to independent $^1$H NMR results and chemical analyses.

The following relationships between unconditional probabilities must hold, irrespective of the sequence statistics:

$$p(\mathrm{V}) + p(\mathrm{E}) = 1 \tag{1}$$

$$p(\mathrm{VV}) + p(\mathrm{VE}) = p(\mathrm{V}) \tag{2}$$

$$p(\mathrm{VEV}) + p(\mathrm{VEE}) = p(\mathrm{VE}) \tag{3}$$

$$p(\mathrm{EEE}) + p(\mathrm{VEE}) = p(\mathrm{EE}) \tag{4}$$

$$p(\mathrm{VE}) = p(\mathrm{EV}) \tag{5}$$

$$p(\mathrm{VEE}) = p(\mathrm{EEV}) \tag{6}$$

These relationships can be used to test the quantitative reliability of the results in Table III (and therefore, by implication, the validity of peak assignments and the assumption of invariant $\eta$), since the triad probabilities were computed from resonances independent of those used to compute the dyad probabilities. The results are in excellent agreement with relations 3 and 4.

The macroscopic copolymer composition, expressed by $p(\mathrm{V})$, was derived from the $^{13}$C NMR data according to relation 2. The results are consistent with the % V values ($100p(\mathrm{V})$) obtained from $^1$H NMR results and chemical analyses (Table III). This agreement provides additional support to the $^{13}$C NMR analysis.

If the reaction of tri-*n*-butyltin hydride with PVB, which converts V units to E units, proceeds in a strictly random fashion, then a Bernoullian distribution of V and E would result at all levels of conversion. The following identities then apply:

$$p(\mathrm{VV}) = p(\mathrm{V})p(\mathrm{V}) \tag{7}$$

$$p(\mathrm{VE}) = p(\mathrm{V})p(\mathrm{E}) \tag{8}$$

with obvious generalization to higher order sequences. The unconditional sequence probabilities computed for a Bernoullian process are shown in parentheses in Table III. These values show no appreciable deviation from the observed compositional sequence probabilities up to the triad level. We may reasonably conclude that the reaction is an ideal random process, where the susceptibility of a V unit to reductive debromination is independent of the identity of its neighboring units.

The question of the influence of stereochemistry on reactivity remains to be considered. The initial PVB had a meso dyad fraction, $p(\mathrm{m})$, of 0.45; i.e., $r/m = 1.22$. After removal of 89% Br, the $r/m$ dyad ratio was 3.0 (this ratio is obtained from the 000101000 resonance pair at 48.78 and 48.58 ppm and independently from the 010100000 resonance pair at 38.64 and 37.36 ppm, as well as the 0101000 pair at 55.8 and 53.7 ppm). Therefore there is a slight preference for m dyads to react; a similar preference has been observed during the reduction of PVC by lithium aluminum hydride.[5]

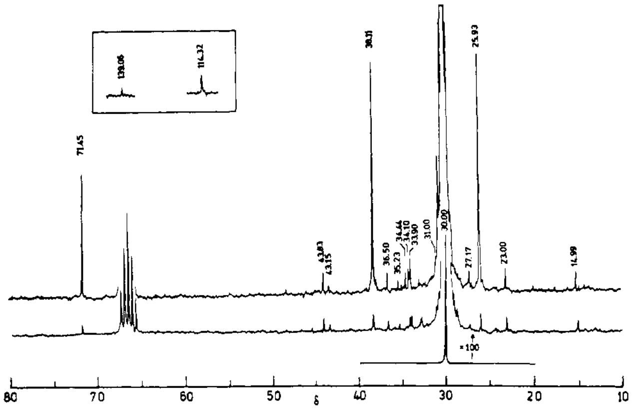


**Figure 5.** 50.3-MHz $^{13}$C NMR spectra of the polyethylenes obtained by complete debromination of a commercial poly(vinyl bromide) (upper trace) and a poly(vinyl bromide) synthesized from pure liquid monomer (lower trace). The pentuplet centered at 66.5 ppm is from dioxane-$d_8$ (internal lock). The inset shows the olefinic resonances observed in the reduced commercial sample (hexachlorobutadiene solution).

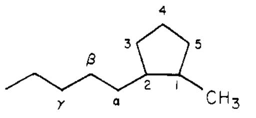
4. **Minor Structural Irregularities in PVB.** In this final section we examine PVB after complete reduction to polyethylene, which results in a considerable simplification of the $^{13}$C NMR spectrum, so that minor irregularities can be clearly discerned and assigned. Figure 5 illustrates these features for two samples, a reduced commercial PVB (upper trace) and a reduced PVB that was initially synthesized in our laboratory by $^{60}$Co $\gamma$ irradiation of pure liquid monomer at 0 °C (lower trace).

The lower limit of detection in these spectra is 0.2 per 1000 carbon atoms. It is apparent that the reduced laboratory sample approximates a linear polymethylene chain very closely, with irregular features not exceeding a level of 2 per 1000 C. The reduced commercial material is quite similar, except for its significantly higher concentration of hydroxyl defects, which will be discussed shortly, and some contaminants from the reduction process. The reduced laboratory sample was further purified by being dissolved and reprecipitated before NMR examination.

Two distinct end groups are detected in approximately equal amounts at a level of 1.5 per 1000 C. One is a terminal double bond, and the other involves a cyclopentyl structure. Since the number-average molecular weight of the reduced commercial PVB is 3700 (270 carbons), its initial and terminal groups should have individual levels of 3.7 per 1000 C. The lower value obtained by $^{13}$C NMR is a consequence of the observation conditions, under which resonances from carbons in the more mobile chain ends are suppressed because their $T_1$ values are comparable to or greater than the 10-s pulse interval.

The terminal double bond generates the olefinic resonances shown in the inset of Figure 5 ($=CH_2$, $\delta$ 114.32; $=CH$, $\delta$ 139.06). The corresponding allylic methylene carbon resonance appears as a shoulder at 33.82 ppm.

The other end group appears to be the *cis*-1-methyl-2-(long alkyl)cyclopentyl moiety I:



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This structure accounts for the rather unusual methyl carbon resonance at 14.99 ppm as well as for the peak observed around 44 ppm. The assigned $\delta$ values are as follows: $CH_3$, 14.99; C(1), 36.50; C(2), 43.83; C(3), 31.00; C(4), 23.00; C(5), 33.90; C($\alpha$), 30.10 (obscured by the major methylene backbone resonance); C($\beta$), C($\gamma$), 30.00 (obscured). These chemical shifts are consistent with values interpolated by means of additivity rules from those reported for *cis*-1,2-dimethylcyclopentyl[6] and *cis*-1-ethyl-2-*n*-nonylcyclopentyl[7] groups. The reduced PVB samples contain 1.5 *cis*-methylcyclopentyl end groups per 1000 C. There are less frequent structures with peaks at 43.15 and 35.23 ppm, which may include C(1) and C($\alpha$) of *trans*-I, respectively, but other resonances to support this assignment were not observed.

Removal of bromine has proceeded to 100% completion. The set of resonances associated with an isolated bromine was not observed in the spectra (Figure 5). The appropriate chemical shifts, obtained from a sample with 3% V, are as follows: $C(\delta)H_2C(\gamma)H_2C(\beta)H_2C(\alpha)HBr$: C($\alpha$), 57.95; C($\beta$), 39.65; C($\gamma$), 27.95; C($\delta$), 29.50.[8] The most prevalent defect resonances are those observed at 71.45, 38.11, and 25.93 ppm in the reduced commercial PVB, which correspond to the $\alpha$, $\beta$, and $\gamma$ carbons, respectively, from the hydroxyl function in the branch structure $C(\gamma)H_2C(\beta)H_2C(\alpha)H(OH)$.[8] These resonance positions were confirmed by the chemical shifts obtained from an ethylene–vinyl alcohol copolymer (2 mol % vinyl alcohol): C($\alpha$), 71.84; C($\beta$), 38.13; C($\gamma$), 25.98; C($\delta$), 29.75 ppm. There are 8.6 OH branches per 1000 C in the reduced commercial PVB, but only 0.6 per 1000 C in the reduced laboratory sample.

No complete set of resonances characteristic of any given *n*-alkyl branch[9] can be observed. The methyl region is devoid of peaks other than the one already assigned at 14.99 ppm. Key resonances for methyl (C($\alpha$), 37.54 ppm), ethyl (CH, 39.68 ppm), propyl (C(3), 36.79 ppm), amyl (CH, 37.86 ppm), and long branches (C($\alpha$), 34.60 ppm) are not observed either. The existence of *n*-butyl branches cannot be dismissed entirely, as peaks are observed at or close to the appropriate shifts ($CH_3$, 14.13; C(2), 23.37; C($\beta$), 27.26; C(4), 34.09; C($\alpha$), 34.44; CH, 38.10 ppm[9]). However, the potential C($\alpha$) and C(4) peaks do not have the necessary 2:1 intensity ratio to substantiate the assignment.

Hydrogen bromide evolves readily from PVB with the formation of internal unsaturation. The olefinic region was examined carefully by $^{13}C$ NMR, using hexachlorobutadiene as the solvent (the usual chlorinated aromatic solvents obscure much of this region). No resonances were detected other than those from the terminal double bond, although this is not too surprising, since internal olefinic carbons are not observed as readily as their neighboring saturated carbons, which have more favorable relaxation times. Thus, the peaks at 32.81 (0.5 per 1000 C) and 27.26 ppm (0.3 per 1000 C) may be the C($\alpha$) resonances from internal trans and cis double bonds, respectively.

Some internal double bonds may react by intramolecular radical addition during the reduction of PVB to form *cis*- and *trans*-1,2-dialkylcyclopentyl rings. These structures and their associated chemical shifts have been reported in the literature.[10] The peaks observed at 23.06, 29.04, 30.33, 31.07, and 43.21 ppm are consistent with the more probable[11] cis structure (0.3 per 1000 C); key resonances for the trans structure (e.g., 46.5 and 24.3 ppm[10]) were not observed.

Hydration of other internal double bonds may take place in the presence of hydrogen bromide to form the hydroxyl groups observed in such significant amounts. These groups are not observed in PVC reduced under similar conditions, however, so a more likely mechanism involves simple nucleophilic substitution of bromine by hydroxide (chlorine is a poorer leaving group than bromine, so substitution would be less favorable in PVC). Since the commercial PVB was prepared in aqueous suspension, it is reasonable that its OH concentration was greater than that of the PVB prepared from pure liquid monomer. The facility of bromine substitution is evident from the fact that the latter polymer was carefully protected from contact with water, except for a brief exposure to atmospheric humidity during preparation of the NMR sample.

The olefinic end group is a consequence of steps involving chain transfer to monomer and termination by disproportionation. The source of a methylcyclopentyl end group is not as obvious, however. A likely pathway[12] begins with the generation of bromine radicals, which add to monomer to initiate chains having a 1,2-dibromo end group. During reduction this vicinal dibromide is converted into an olefin,[13] which can undergo an intramolecular cyclization with the radical generated after removal of bromine at the 6 position. The preferred isomer[11] after cyclization is the *cis*-1-methyl-2-(long alkyl)cyclopentane isomer, as confirmed by the $^{13}C$ NMR spectra.

The negligible concentration of *n*-alkyl branches in PVB after reduction contrasts with the branch microstructure of PVC.[14] The *n*-alkyl branches in reduced PVC originate from head–head monomer additions and intramolecular radical back-biting steps.[15] Both processes are less likely during polymerization of vinyl bromide, owing to the more severe steric constraints imposed by the larger bromine substituent.

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usually denotes the main-chain carbon next to the branch carbon as α.[9]
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# Analysis of the Mechanism of Copolymerization of Styrene and Acrylonitrile

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ABSTRACT: The copolymerization of styrene and acrylonitrile in bulk at 60 °C has been investigated by measurement of the copolymer/comonomer composition relationship and of the monomer sequence distributions using $^{13}$C NMR. Alternative models for the mechanism of the copolymerization have been evaluated in the most general forms, with allowance for nonzero conversions, by deriving reactivity ratios from composition data and then comparing predicted and experimental sequence distributions. The system shows significant deviations from the terminal model. Compositions cannot differentiate between penultimate and complex participation models, both of which give significant improvement over the terminal model. The measured sequence distributions are quite close to the predictions of the penultimate model but substantially different from those of the complex participation model, showing clearly that the penultimate model is the most appropriate of the models considered. We have obtained $r_{SS} = 0.22_9$, $r_{AA} = 0.03_9$, $r_{AS} = 0.63_4$, and $r_{SA} = 0.09_1$. No significant improvement was observed with the antepenultimate model.

## Introduction

There have been numerous studies of the copolymerization of styrene (S) and acrylonitrile (A). The terminal model for copolymerization has frequently been assumed to apply and values for the two reactivity ratios have been derived. Sandner and Loth[1] have recently summarized the reported values. However, some workers have interpreted their copolymer/comonomer composition relationships as deviating from the terminal model and considered the applicability of more sophisticated mechanisms. Thus, Ham[2] in 1954 interpreted apparent deviations from the terminal model on the basis of penultimate effects. Guyot and Guillot (1967–1968)[3,4] reported the necessity to introduce both penultimate and antepenultimate effects to describe their data for the copolymerization in dimethylformamide and toluene solutions. More recently, Sandner and Loth (1976)[1] investigated the bulk copolymerization and claimed that penultimate and antepenultimate effects were not the actual causes of deviation from the terminal model. Sandner et al. also reported[5] an equilibrium constant, $K_x$ (≈0.5), for the formation of a 1:1 comonomer complex at 60 °C (concentrations in mole fractions) and suggested that complex participation was involved in the copolymerization. Kucher et al.[6] have presented a kinetic treatment for the copolymerization from which they deduce that the experimental rates of polymerization can be fitted by participation of a comonomer complex, which is 8 and 13 times more reactive in propagation than styrene and acrylonitrile, respectively.

Since Seiner and Litt[7] published the first mathematical analysis of the complex participation model for copolymerization in 1971, it has been possible to evaluate quantitatively whether this model is appropriate to a particular copolymerization. Most studies have used limitations on the model for calculating the reactivity ratios in order to avoid the complicated expression for copolymer composition developed by Seiner and Litt. However, Pittman and Rounsefell[8] demonstrated that the reactivity ratios and the equilibrium constant for complex formation could be obtained by computer techniques using the unrestricted form of Seiner and Litt's equation.

Recently, we reported an alternative to Seiner and Litt's method of analysis of the complex participation model.[9] Moreover, we have demonstrated how the monomer sequence distribution in the copolymer as well as the copolymer composition can be related to the equilibrium constant, six different reactivity ratios, and the comonomer feed composition.

Most investigations for the mechanism of copolymerization involve an analysis of the composition of the initial copolymers formed, but it is often difficult to distinguish between the various models for copolymerization on the basis of their fit to the composition data alone. The distribution of monomer sequences in the copolymer contains more information about the polymerization system than the copolymer composition (although the sequence distributions cannot be determined at present with the same accuracy). This information, together with copolymer composition for copolymers prepared over the range of comonomer composition, should discriminate between the terminal, penultimate, and complex participation models. Recent developments in the characterization of polymer microstructure mean that sequence distributions can be obtained for a variety of copolymers.

In a recent analysis of the acrylonitrile–styrene copolymerization system, we demonstrated[10] that, by using sequence distribution information, it would be possible to distinguish between the penultimate and complex participation models, both of which could explain the polymer composition data.

The sequence distributions of acrylonitrile–styrene copolymers were analyzed by $^{13}$C NMR spectroscopy by Schaefer (1971)[11] and Stejskal and Schaefer (1974),[12] who determined triad fractions and number-average sequence lengths. Subsequently, Sandner and co-workers[13] analyzed the spectra for dyad fractions as well as styrene- and acrylonitrile-centered triad fractions. Recently, Pichot and

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