energy surfaces of PP will be required to account for the stereochemical dependence of $T_1$.

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# Calculated Carbon-13 Nuclear Magnetic Resonance Chemical Shifts for Ethylene–Vinyl Chloride Copolymers

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ABSTRACT: $^{13}$C NMR chemical shifts expected for the carbon atoms in ethylene–vinyl chloride (E–VC) copolymers are calculated as functions of the E and VC monomer sequence distribution and the stereoregularity of the VC sequences. The $\gamma$ gauche effect, which results in upfield chemical shifts for those carbon atoms in a gauche arrangement with carbon or chlorine substituents in the $\gamma$ position, is utilized, together with the predicted bond rotational state probabilities obtained from Mark's conformational model of E–VC copolymers, to calculate the $^{13}$C NMR chemical shifts for carbons in the various microstructural environments possible in E–VC copolymers. The methine and methylene carbon chemical shifts are predicted to occur over $\sim$6- and $\sim$30-ppm ranges, respectively, solely as a result of different monomer sequence distributions. The several-fold greater range of methylene carbon chemical shifts is due to the downfield shift produced by the presence of different numbers of deshielding chlorine atoms in the $\beta$ position. In nearly all cases the effects of monomer sequence distribution and stereosequence are clearly separable and should be experimentally resolvable. The predicted chemical shifts are in excellent agreement with the $^{13}$C NMR spectra reported by Keller and Mugge for chlorinated polyethylene and observed by one of us for reduced poly(vinyl chloride).

## Introduction

$^{13}$C NMR spectroscopy[1-3] is currently the most powerful probe of polymer microstructure. The utility of this spectroscopic method is a consequence of the extreme sensitivity of the observed $^{13}$C chemical shifts to local elements of polymer structure, such as sequence of comonomer units,[2,3] stereoregularity,[3] inverted monomer addition,[4] branching,[5] etc. Recently[6] the full potential of structural information contained in the $^{13}$C chemical shifts observed for synthetic polymers has been realized through our ability to predict the relative chemical shifts produced by different polymer microstructures.

The relative chemical shifts of a carbon atom depends on the number and kinds of substituents attached to it. $^{13}$C NMR studies[7-10] of hydrocarbons and their derivatives have established substituent rules which can be used to produce accurate estimates of the observed chemical shifts. As an example, each carbon substituent $\alpha$ or $\beta$ to the observed carbon produces a downfield shift (deshielding effect) of ca. +9 ppm relative to an unsubstituted carbon. By contrast each carbon $\gamma$ substituent yields an upfield shift (shielding effect) of ca. $-2$ to $-3$ ppm.

The shielding effect produced by a $\gamma$ substituent has been demonstrated[6,11-17] to require a gauche arrangement between the observed and substituent carbons (see Figure 1). The frequency of such $\gamma$ gauche arrangements depends on the microstructure of the polymer in the vicinity of the observed carbon. It is possible to evaluate the frequency of $\gamma$ gauche interactions and the resultant relative $^{13}$C chemical shifts from a knowledge of the polymer chain conformational characteristics and the magnitude of the upfield shift produced by each $\gamma$ gauche interaction.

This approach[6] has been successfully applied to predict the $^{13}$C NMR chemical shifts expected for the various carbon atoms in polypropylene[18] and its oligomers,[12,15] ethylene–propylene copolymers,[13,17] poly(vinyl chloride)[14] and its oligomers,[14] the oligomers of polystyrene,[16] and several fluorinated polymers.[19] The effects of stereosequence, comonomer distribution, and defect structures have all been successfully accounted for, thereby providing detailed microstructural descriptions of these polymers. In the present work we extend this approach to the copolymers of ethylene and vinyl chloride (E–VC).

## Calculation of $^{13}$C NMR Chemical Shifts

Mark's[20] rotational isomeric states model of E–VC copolymers is used to calculate[21] bond rotation probabilities necessary to the evaluation of the number of $\gamma$ gauche interactions involving a given carbon atom. On the basis of our previous studies,[14] we adopt the following $\gamma$ gauche

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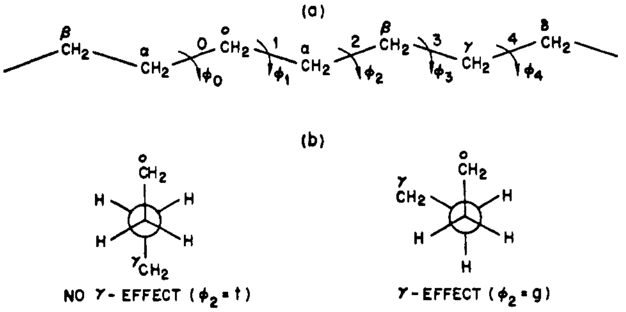

**Figure 1.** (a) Portion of a paraffinic hydrocarbon chain in the all-trans, planar zigzag conformation. (b) Newman projections along bond 2 in a illustrating the $\gamma$ gauche effect.

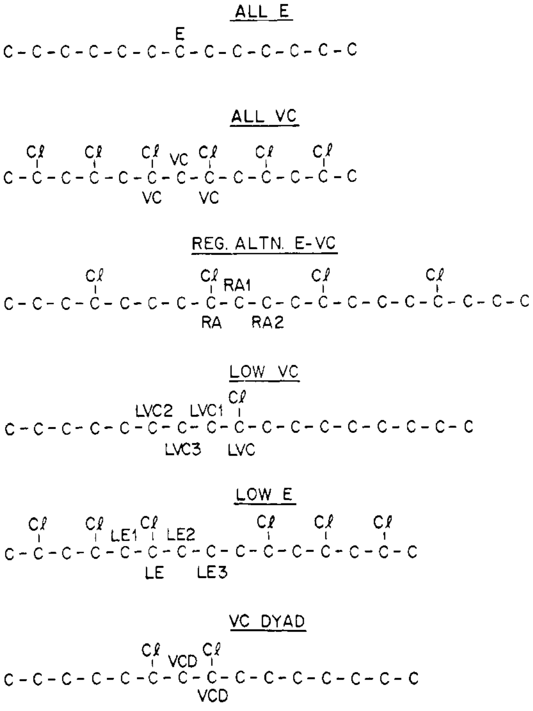

**Figure 2.** Possible microstructures in E–VC copolymers produced by head-to-tail addition of monomer units.

upfield chemical shifts, where $\gamma_{a,b}$ is the upfield shift at carbon a produced by $\gamma$ substituent b when in a gauche arrangement: $\gamma_{\mathrm{CH\ or\ CH_2,CH_2}} = -5$ ppm; $\gamma_{\mathrm{CH_2,CH}} = -2.5$ ppm; $\gamma_{\mathrm{CH\ or\ CH_2,Cl}} = -3$ ppm.

In addition to $\gamma$ effects, methylene carbons in certain monomer sequences (see Figure 2) possess different numbers of chlorine atom substituents in the $\beta$ position, which can affect their chemical shifts. From $^{13}$C NMR studies[22] of chlorinated paraffins, the presence of a single chlorine substituent in the $\beta$ position is observed to produce a downfield shift of +10.5 ppm, while 2$\beta$-Cl's result in a +19.5-ppm deshielding. We adopt $\beta_{\mathrm{Cl}} = +10.5$ ppm and $\beta_{\mathrm{2Cl}} = +19.5$ ppm in evaluating the relative chemical shifts of the methylene carbons in E–VC copolymers.

In addition to calculating the chemical shifts of the carbon atoms in the parent homopolymers polyethylene and poly(vinyl chloride) (PVC), we consider regularly alternating E–VC and E–VC copolymers with very low contents of either ethylene or vinyl chloride units. In all E–VC copolymers where two or more consecutive VC units occur, the effects of the stereosequence of these units is taken explicitly into account when calculating the $^{13}$C NMR chemical shifts of nearby methine and methylene carbons. All monomer units are assumed to be incorporated exclusively in the head-to-tail manner and the presence of chain branching is ignored.

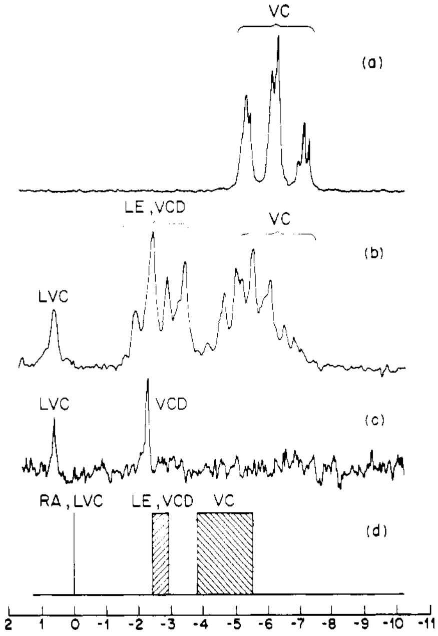

**Figure 3.** (a) 25.16-MHz $^{13}$C NMR spectrum (methine carbon region) of atactic PVC observed[27] at 107 °C, using a 10% (w/v) solution in 1,2,4-trichlorobenzene. Addition of 62.5 ppm yields chemical shifts relative to $Me_4Si$. (b) Same as a except 29% thiol-reduced PVC.[25] (c) Same as a except 99.6% $LiAlH_4$-reduced PVC.[26] (d) $^{13}$C chemical shifts calculated at 100 °C for the methine carbons residing in the E–VC microstructures of Figure 2. The widths of the resonances result from chemical shift dispersion produced by the stereoregularity of VC units.

## Results and Discussion

Figure 2 contains schematic drawings of the various E–VC homo- and copolymers treated in the present study, with those methine and methylene carbons whose calculated $^{13}$C NMR chemical shifts are unique possessing labels. $^{13}$C NMR chemical shifts calculated at 100 °C for the methine and methylene carbons in E–VC copolymers are presented in Figures 3d and 4c, where the width of each CH and $CH_2$ resonance represents the calculated dispersion in chemical shift due to VC stereoregularity.

The calculated chemical shifts do not distinguish between the methine carbons in regularly alternating and low-VC E–VC copolymers (see Figures 2 and 3d). Two to three parts per million upfield from the resonance for these methine carbons come the resonances for the methine carbons in an isolated VC dyad and the terminal methines in low-E E–VC copolymers, which again cannot be distinguished from each other. These midfield peaks show a 0.5-ppm dispersion in chemical shift due to VC stereosequence. Finally at higher field come the resonances for the methine carbons in long VC sequences with a chemical shift dispersion of ca. 1.7 ppm due to VC stereoregularity.[14] Summarizing, the methine carbon resonances in E–VC copolymers are predicted to occur in three well-separated regions encompassing nearly 6 ppm in overall spread due to monomer sequence distribution.

In contrast to the $^{13}$C chemical shifts calculated for the methine carbons, the methylene carbons in long VC sequences are expected to resonate most downfield with a 2.4-ppm dispersion due to VC stereosequence.[14] Ten other methylene carbons (see Figures 2 and 4c) have chemical shifts calculated to be as much as −25 to −30 ppm upfield from the all-VC peaks. With the possible exception of the

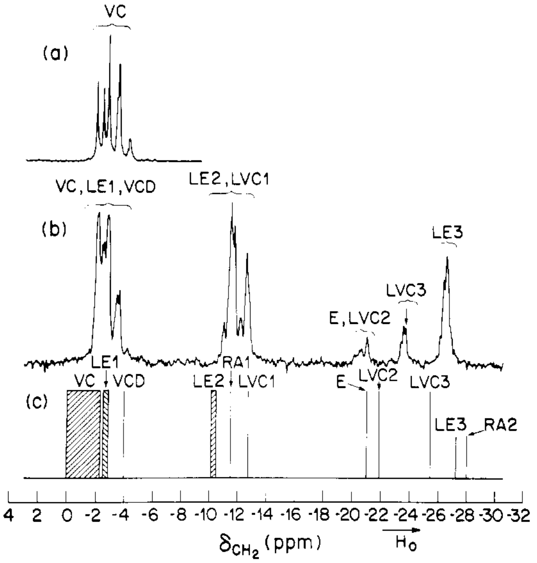

**Figure 4.** (a) Same as Figure 3a except methylene carbon region. (b) Same as Figure 3b except methylene carbon region. (c) $^{13}C$ chemical shifts calculated at 100 °C for the methylene carbons residing in the E–VC microstructures of Figure 2. The widths of the resonances result from chemical shift dispersion produced by the stereoregularity of VC units. Although the absolute heights or intensities of the resonances are arbitrary, it is clear from Figure 2 that the intensities of LVC1, -2, and -3 should be equal, LE1 = LE2 = 2(LE3), and RA1 = 2(RA2).

LE1 methylene resonance (see Figures 2 and 4c), the chemical shifts of each of the methylene carbons in E–VC copolymers are well separated. In addition, only the all-VC peak is significantly influenced by VC stereoregularity.

The fivefold greater spread calculated for the methylene carbon chemical shifts is attributable to the presence or absence of Cl substituents in the $\beta$ position. Depending on monomer sequence, a methylene carbon can be $\beta$ to 0, 1, or 2 Cl atoms, resulting[22] in relative downfield chemical shifts of 0, +10.5, or +19.5 ppm, respectively. Still over 8 ppm in the total methylene carbon chemical shift spread is due to differences in amount and kind of $\gamma$ gauche interactions experienced by methylene carbons in the various microenvironments produced by different E–VC monomer sequences.

From the calculated chemical shifts it appears that both types of carbons (methine and methylene) can be fruitfully studied by $^{13}C$ NMR to determine the microstructures of E–VC copolymers. However, it is apparent that the $^{13}C$ chemical shifts of the methylene carbons are predicted to show a greater sensitivity to E–VC monomer sequence than the methine carbons, due principally to differences in the number of $\beta$-Cl substituents[22] possessed by methylene carbons in the various monomer sequences constituting the microstructure of E–VC copolymers.

Keller and Mugge[23] have reported $^{13}C$ chemical shifts of the methine and methylene carbons in a series of chlorinated polyethylenes. They observe[24] three peaks at 0, −3, and −7 ppm in the methine carbon region, in excellent agreement with the three distinct calculated chemical shifts seen in Figure 3d. In the methylene carbon region they report prominent resonances at −4, −13, −22, −25, and −28 ppm. Comparison with the calculated $^{13}C$ chemical shifts displayed in Figure 4c reveals good agreement between the methylene resonances observed[23] in chlorinated polyethylene and those predicted for E–VC copolymers.

The methine carbon regions of the $^{13}C$ NMR spectra of atactic PVC[27] and two samples of reduced PVC[25,26] are presented in Figure 3a–c. Note the close correspondence between observed and predicted $^{13}C$ chemical shifts both in regard to resonance position and sensitivity to VC stereosequence. Similar agreement between observed and calculated $^{13}C$ chemical shifts is achieved for the methylene carbons in PVC and E–VC (reduced PVC)[25] copolymers as seen in the comparison presented in Figure 4a–c.

The favorable comparison between observed and calculated $^{13}C$ chemical shifts in E–VC copolymers confirms the $\gamma$ effects derived from our study[14] of poly(vinyl chloride) and its oligomers and the conformational model of E–VC copolymers[28] developed by Mark.[20] It would appear that the calculated chemical shifts presented in Figures 3 and 4 can be compared with the $^{13}C$ NMR spectra of E–VC copolymers to determine their microstructural details.

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