^{13}C NMR Spectroscopy as a Means To Probe the Local Microstructures and Conformations of Ethylene–Vinyl Acetate Copolymers

E. Tart, G. Wood, D. Wernsman, U. Sangwatanaroj, C. Howe, Q. Zhou, S. Zhang, and A. E. Tonelli*

Fiber + Polymer Science Program, College of Textiles, North Carolina State University, Raleigh, North Carolina 27695-8301

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ABSTRACT: A recently developed conformational description (RIS model) of ethylene–vinyl acetate (E–VAc) copolymers, obtained by merging the RIS models of the constituent homopolymers, is used to calculate microstructurally sensitive ^{13}C chemical shifts expected from the high-resolution, solution ^{13}C NMR spectra recorded for the complete range of E–VAc copolymers. Microstructurally sensitive ^{13}C resonance frequencies and local E–VAc conformations are connected via conformationally sensitive γ-gauche shielding effects. Comonomer sequences to the pentad level and VAc stereosequences to the pentad (methine carbons) and hexad (methylene carbons) levels are considered. Calculated ^{13}C chemical shifts are found to be in close agreement with those observed and assigned previously for a series of E–VAc copolymers by Wu et al. and Sung and Noggle. In addition the ^{13}C chemical shifts calculated for the various stereosequences in atactic PVAc compare favorably to the observed spectrum of the atactic homopolymer and facilitate its assignment. The successful comparison of calculated and observed ^{13}C chemical shifts in E–VAc copolymers validates the conformational RIS model recently developed for this copolymer. This conformational validation rests on our ability to predict the microstructurally sensitive local bond conformations in E–VAc copolymers rather than upon traditional global measures of polymer conformations, such as the mean-square end-to-end distances and dipole moments.

Introduction

Poly(vinyl acetate) (PVAc) and ethylene–vinyl acetate (E–VAc) copolymers are commercially significant, and their ^1H and ^{13}C NMR spectra have been repeatedly recorded[1-11] and used to establish their microstructures, i.e., comonomer and stereosequence distributions. By combination of observations made at high magnetic field[6,10] with comparisons to the spectra recorded[1] for an extensive series of E–VAc model compounds (mono- and diacetates of aliphatic alcohols and diols), the microstructures of the complete range of E–VAc copolymers have been reasonably well characterized.

In addition, a conformational description (RIS model)[12] of E–VAc copolymers has recently been developed[13] by merging the RIS models of the constituent homopolymers PE[14] and PVAc.[15] The copolymer RIS model was employed to calculate[12] the dimensions (mean-square end-to-end distances) and dipole moments as a function of E–VAc microstructure. However, only the dimensions of the constituent homopolymers PE and atactic PVAc and the dipole moments of atactic PVAc have been measured, so to date the conformational characteristics of E–VAc copolymers as predicted from their RIS model have not been thoroughly tested.

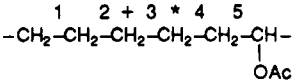
We have noted[16] that the sensitivity of the ^{13}C NMR solution spectra of vinyl homo- and copolymers to their microstructures can be usefully connected to their microstructurally sensitive local conformations via the γ-gauche effect.[16,17] Now that a conformational description in the form of a RIS model has been developed for E–VAc copolymers,[13] we are in a position to employ the conformationally sensitive γ-gauche effect method to predict the ^{13}C chemical shifts of all microstructurally distinct carbons in these copolymers. By comparing the ^{13}C chemical shifts calculated from the E–VAc RIS model via the γ-gauche effect method to the ^{13}C NMR spectra observed for these copolymers, we may assess the validity of the RIS model recently developed[13] for E–VAc copolymers.

Calculation of ^{13}C NMR Chemical Shifts in E–VAc Copolymers

The statistical weight matrices appropriate to the calculation[12] of bond conformation probabilities in E–VAc copolymers have been derived and described recently.[13] With these conformational probabilities or populations we may calculate the number of gauche conformational arrangements between any of the E–VAc backbone carbons and their nonprotonic γ-substituents separated by three intervening bonds. We consider only the backbone methine and methylene carbons, because it is these portions of the ^{13}C NMR spectra of E–VAc copolymers which previously have been extensively assigned[1,10] to their microstructures and because it is the backbone conformations of the copolymers which both determine the γ-gauche shielding experienced by them and constitute the E–VAc RIS model.

We have considered E–VAc comonomer sequences to the pentad level and consecutive VAc stereosequences to the pentad (methine carbons) and hexad (methylene carbons) levels. Based on the observations and assignments of Sung and Noggle,[10] we have also assumed the absence of any H–H:T–T addition of monomer units in the E–VAc copolymers.

We illustrate the ^{13}C chemical shift calculations by means of several examples concerning the methylene carbons. In the EEVAc triad comonomer sequence



the CH_2^+ and CH_2^* methylene carbons have calculated ^{13}C chemical shifts given by $\delta CH_2^+ = (2.0 - P_{1,t} - P_{4,t})\gamma_{c,c}$ and $\delta CH_2^* = (2.0 - P_{2,t} - P_{5,t})\gamma_{c,c} + (1.0 - P_{5,g\pm})\gamma_{c,o}$, where $P_{i,t \text{ or } g\pm}$ is the probability of finding bond i in the t or g± conformations and $\gamma_{c,c}$ and $\gamma_{c,o}$ are the shielding produced at methylene carbon nuclei by C and O γ-substituents in a gauche conformational arrangement.

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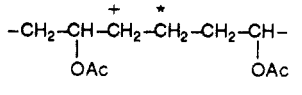
In addition to γ-gauche or conformational differences produced by different E–VAc microstructures, methylene carbons may be β to acetyl O atoms, which is expected[1,18] to deshield them, in certain E–VAc microstructures. In EEE and EEVAc triads both methylene carbons of the central E unit have no β-O's. One of the methylene carbons in the central units of VAcEE and VAcEVAc triads and the VAc methylene carbon in EVAcE, VAcVAcE, and EVAcVAc triads have a single β-O, while the central methylene carbons in VAcVAcVAc triads have 2 β-O's. The conformationally-independent deshielding of methylene carbons by β-O substituents was accounted for by assuming[1,16,18] that each β-O substituent deshields a methylene carbon nucleus by +5 ppm.

A deshielding of +5 ppm by a β-O substituent is consistent with the value derived by Wu et al.[1] from their ^{13}C NMR observations of E–VAc model compounds and also corresponds to the observed difference[1,10] in resonance frequencies between E–VAc methylene carbons that have nearly identical γ-gauche shieldings, but with different numbers of β-O substituents. For example, the methylene carbons in the central VAc unit of the EVAcVAc comonomer triad is β to 1 acetyl O, while the methylene carbon in the central VAc unit of the VAcVAcE comonomer triad is β to 2 acetyl O's. However, both methylene carbons possess nearly the same number of γ-gauche arrangements with backbone carbons. Thus we would expect the central VAc methylene carbons in EVAcVAc triads to resonate upfield from the central VAc methylene carbons in VAcVAcE triads by (1 β-O − 2 β-O's) = −1 β-O effect. Experimentally this separation is found to be ca. −5 ppm, so β-O = +5 ppm is adopted in our ^{13}C NMR chemical shift calculations. Independent of E–VAc microstructure, all methine carbons have two backbone carbon β-substituents.

The magnetic shielding experienced by methylene and methine carbon nuclei when in gauche arrangements with C and O γ-substituents is expected[1,15,18] to be in the range −3 to −7 ppm. We have found that for both backbone nuclei in E–VAc copolymers $\gamma_{c,o}$ = −3 ppm and $\gamma_{c,c}$ = −5 ppm lead to calculated ^{13}C-13 chemical shifts in good agreement[19] with their observed ^{13}C NMR spectra.

Results and Discussion

The ^{13}C NMR spectrum recorded for a 60/40 E–VAc copolymer at 62.86 MHz by Sung and Noggle[10] on a 10 wt % $CDCl_3$ solution at 50 °C is presented in Figure 1, where only the methylene and methine carbon portions of the spectrum are drawn. The nomenclature used[1,9,10] to label the methylene carbon region of the spectrum signifies the positions of nearest –OAc side groups. For example, in the VAcEVAc triad the C^+H_2 methylene is βδ and the



CH_2* methylene is γγ to their nearest –OAc side groups. In Figures 2 and 3 the observed and calculated ^{13}C chemical shifts of the methine and methylene carbon nuclei in E–VAc copolymers are compared. The methylene and methine carbon regions of the 62.86-MHz ^{13}C NMR spectrum of atactic PVAc recorded by Sung and Noggle[10] are reproduced in Figure 4, and in Figures 5 and 6 the calculated and observed methylene and methine ^{13}C chemical shifts are compared. Note the generally close agreement in Figures 2 and 3 between the observed and

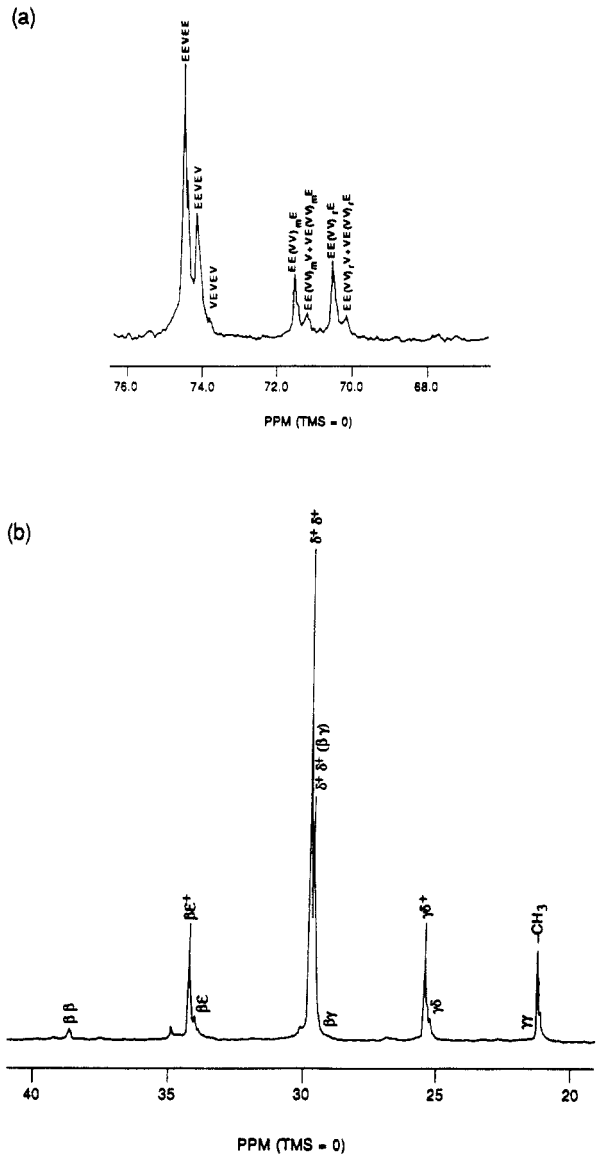


Figure 1. The 62.86-MHz ^{13}C NMR spectrum of a 60/40 E–VAc copolymer recorded and assigned by Sung and Noggle:[10] (a) methine region; (b) methylene region.

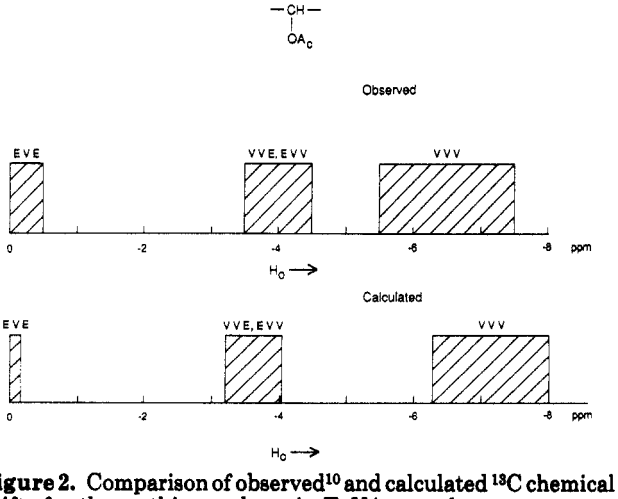


Figure 2. Comparison of observed[10] and calculated ^{13}C chemical shifts for the methine carbons in E–VAc copolymers.

calculated ^{13}C chemical shifts for the methylene and methine carbons residing in the various E–VAc microstructures.

Let us examine more closely both backbone carbon regions of the E–VAc observed spectrum in Figure 1. Wu et al.[1] and Sung and Noggle[10] both assign the EVAcE

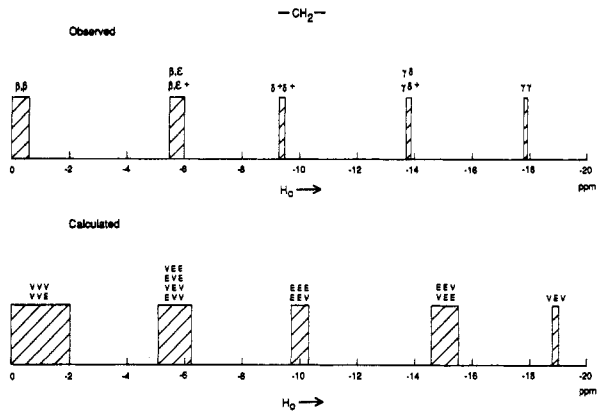


Figure 3. Comparison of observed[10] and calculated ^{13}C chemical shifts for the methylene carbons in E–VAc copolymers.

methine resonances centered at 74.5 ppm to the E(EVAcE)E, E(EVAcE)VAc, and VAc(EVAcE)VAc comonomer sequences from low to high field, respectively. We find the probabilities of gauche arrangements between EVAcE-centered methine carbons and their γ-methylene carbon substituents to be 0.288, 0.292 (0.294), and 0.296 (0.300) for the E(EVAcE)E, E(EVAcE)VAc (m and r across E), and VAc(EVAcE)VAc (mm and rr across E's), which agree with the observed order of these methine resonances.

Two groups of EVAcVAc-centered methine carbon signals at ca. 71.5 and 70.5 ppm are observed in Figure 1, with the lower field group assigned to m-VAcVAc diads and the higher field group to r-VAcVAc diads. This assignment agrees with the ^{13}C chemical shifts calculated for the EVAcVAc triad centered E–VAc microstructures. The bond conformational probabilities indicate that in r-VAcVAc diads the population of γ-gauche arrangements between CH and OAc is greater than that between CH and CH_2-, while the opposite is true for the m-VAcVAc diads. Because $\gamma_{c,o} = -5$ ppm and $\gamma_{c,o} = -3$ ppm, the shielding of the methine carbons in r-VAcVAc diads exceeds that expected for a m-VAcVAc diad. Beyond the m or r character of the VAcVAc diad, differences in γ-gauche shielding probabilities calculated for different pentad comonomer sequences all with the common EVAcVAc or VAcVAcE triad sequences are too small to permit us to comment on Sung and Noggle's[10] detailed assignments in the methine carbon region of the E–VAc copolymer spectrum.

We will discuss the VAcVAcVAc-centered methine carbon region when we compare the calculated and observed ^{13}C chemical shifts for the atactic PVAc homopolymer.

Moving to the methylene carbon region of the E–VAc spectra shown in Figures 1 (observed) and 3 (observed and calculated), it is apparent that both the experimental and calculated assignments coincide. The methylene carbons in each of the E–VAc comonomer triads labeling the calculated chemical shifts may be characterized by exactly the same positions of neighboring –OAc groups as denoted by the peaks in the observed spectrum. As an example, the methylene carbons in the central units of VAcEE, EVAcE, VAcEVAc, and EVAcVAc comonomer triads all have single β-OAc and single ϵ or ϵ^+-OAc substituents.

The observed and calculated ^{13}C NMR spectra of atactic PVAc are seen in Figures 4–6. Note that in the methylene carbon regions compared in Figure 5 both the observed and calculated order of resonances is rxr, mxr (rxm), mxm from low to high field. However, the m-centered tetrads are observed upfield from the corresponding r-centered

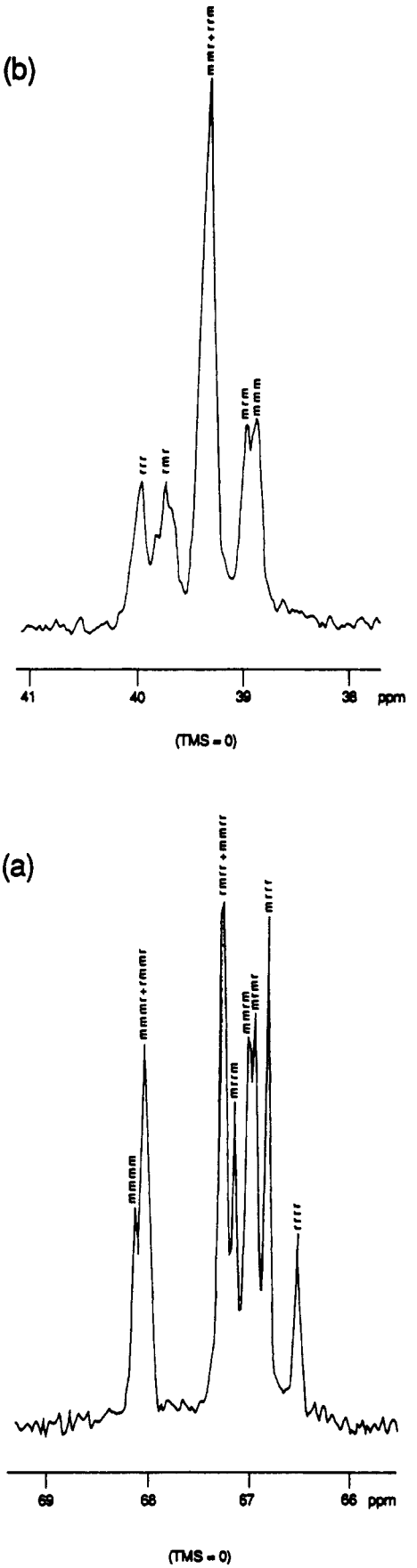


Figure 4. The 62.86-MHz ^{13}C NMR spectrum of atactic PVAc recorded and assigned by Sung and Noggle:[10] (a) methine region; (b) methylene region.

tetrads in the observed spectrum, while the opposite behavior is evidenced by the calculated methylene carbon chemical shifts. It should be mentioned that the calculated tetrad methylene carbon chemical shifts are averaged over

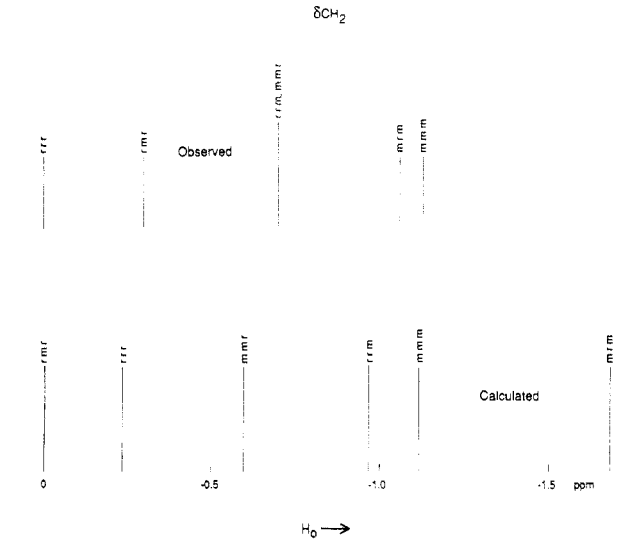


Figure 5. Comparison of observed[10] and calculated ^{13}C chemical shifts for the methylene carbons in atactic PVAc.

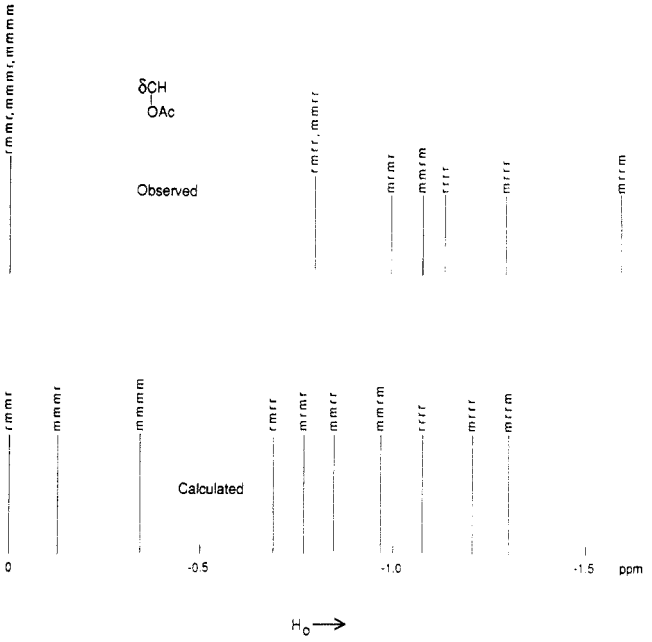


Figure 6. Comparison of observed[10] and calculated ^{13}C chemical shifts for the methine carbons in atactic PVAc.

all hexads containing common tetrad stereosequences. Perhaps it is not surprising that the tetrad methylene carbon chemical shifts in atactic PVAc are more sensitive to the stereochemistry of the terminal diads than the m or r character of the central diad. After all, the terminal diads contain the backbone bonds which govern whether or not the methylene carbon is gauche to the terminal carbons in the tetrad, and we should expect their gauche: trans conformational ratios to be highly sensitive to the stereochemistry of the terminal diads.

The observed and calculated methine carbon chemical shifts compared in Figure 6 are seen to be in general agreement. Sung and Noggle[10] were unable to unambiguously assign mrmr, rrrr, and mrrm stereosequence pentads, so we have taken the liberty to assign them in this order with increasing field strength to make them consistent with our calculated methine carbon chemical shifts. The ability to calculate the stereosequence-dependent ^{13}C chemical shifts in vinyl polymers substantially aids the assignment of their ^{13}C NMR spectra particularly when they are stereochemically random ($P_m \sim P_r \sim 0.5$), like the atactic PVAc sample observed by Sung and Noggle[10] ($P_m = 0.48$), and all stereosequences appear with nearly equal intensities in the spectrum.

Because the diads constituting the central triad stereosequences in each PVAc pentad contain the backbone bonds whose conformations determine whether or not the methine carbon is gauche to its CH_2 and OAc γ-substituents, it is not surprising that their *x*mm*y*, *x*mr*y*(*x*rm*y*), or *x*rr*y* character affects the methine carbon resonance frequencies much more sensitively than the stereochemistry of the terminal diads m*x*y*m*, m*x*y*r*(r*x*y*m*), or r*x*y*r* in each pentad. This expectation is borne out in both the observed and calculated methine carbon spectra and is a consequence of the conformational origin (γ-gauche effect)[16,17] of their stereochemical sensitivity.

The generally good overall agreement between the ^{13}C NMR spectra observed for E–VAc copolymers with their calculated ^{13}C chemical shifts presented here lends strong support to the conformational description/RIS model employed for the E–VAc copolymers.[13] Only three shielding parameters were used to calculate the chemical shifts, β-OAc = +5 ppm, $\gamma_{c,c} = -3$ ppm, and $\gamma_{c,o} = -5$ ppm, and β-OAc = +5 ppm had been previously determined by Wu et al.[1] from the ^{13}C-13 NMR spectra of E–VAc model compounds. Our ability to calculate microstructurally sensitive ^{13}C NMR chemical shifts in E–VAc copolymers not only aids the assignment of their spectra but illustrates the potential for testing and/or deriving conformational RIS models for vinyl homo- and copolymers by comparing their observed ^{13}C NMR spectra with ^{13}C chemical shifts calculated via the conformationally sensitive γ-gauche effect method.

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