The agreement of the various concentrations at the highest temperatures strongly suggests that the second virial coefficient is indeed near zero there as well as at room temperature. However, even an unrealistically high second virial coefficient would not be sufficient, at these concentrations, to force a material change in these results. Even if the second virial coefficient at, say, 60 °C were as high as it is at room temperature in 5 M guanidinium chloride (7.13×10^{-4} mol cm^3 g^{-2}),[5] it would increase the molecular weight given in Figure 2 for the sample of highest concentration by less than 6%. To produce a change comparable to the experimental error, a second virial coefficient of $\sim 14 \times 10^{-4}$ mol cm^3 g^{-2}—an unheard of value—would be required. The assumption that the second virial coefficient can be ignored over the entire temperature range is clearly justified.

The hatched band drawn on Figure 2 shows the previously published (Figure 7 of ref 16) prediction of weight-average aggregation number made from a statistical mechanical theory of the helix–coil transition; this prediction is shown as corrected for mass action to the concentration range of our light scattering experiments. Although recent advances in the theory[31-33] make it unwise to make a detailed comparison of our data with this relatively unsophisticated earlier version, it seems safe to say that the principal qualitative theoretical prediction—that loss of helix content and chain dissociation go hand-in-hand—is strikingly borne out. This close linkage is by no means generally accepted at present; at least two laboratories much concerned with these matters would center the dissociation at rather higher temperature than the loss of helix.[13,19] Whether the present data are compatible in more quantitative detail with the current, more sophisticated form of the theory remains to be seen. In any event, we now have two independent physical characteristics of the transition, helix content and weight-average aggregation number, to guide our understanding.

Acknowledgment. Gratitude is hereby expressed to the Japan Society for Promotion of Science, whose award to A.H. of a Fellowship for Research in Japan made this collaboration possible. The hospitality of Nagoya University and of the Nagasawa Coza is also acknowledged. Part of this work was also supported by Grant No. GM-20064 from the Division of General Medical Sciences, U.S. Public Health Service.

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Carbon-13 Nuclear Magnetic Resonance Chemical Shifts of Poly(vinyl alcohol)

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ABSTRACT: ^{13}C NMR chemical shifts are calculated for the carbon nuclei in poly(vinyl alcohol) (PVOH) to the pentad and hexad levels of stereosequence for the methine and methylene carbons, respectively. This is achieved through utilization of the conformationally sensitive γ-gauche effect method which accounts for the magnetic shielding of those carbons in a gauche arrangement with their γ substituents. The RIS model of PVOH developed by Wolf and Suter is employed to calculate the frequencies of γ-gauche arrangements between methylene and methine carbons and between hydroxyl groups and methine carbons. Calculated chemical shifts are compared to the 100-MHz ^{13}C NMR spectra reported for PVOH in D_2O and dimethyl-d_6 sulfoxide by Ovenall. The relative orders of the observed methine pentad and methylene hexad ^{13}C resonances agree with the calculated chemical shifts, in addition to agreement between the overall chemical shift dispersions measured and predicted for the methylene carbons. However, the 3–4 ppm spread observed for the methine resonances is severalfold larger than the dispersion in chemical shifts calculated for the methine carbons.

Introduction

The microstructural dependence of the ^{13}C NMR spectra of vinyl polymers has been demonstrated to have a conformational origin.[1] Polymer microstructure affects the local conformations[2-5] of the polymer chain, which in turn determine the magnetic fields experienced by its carbon

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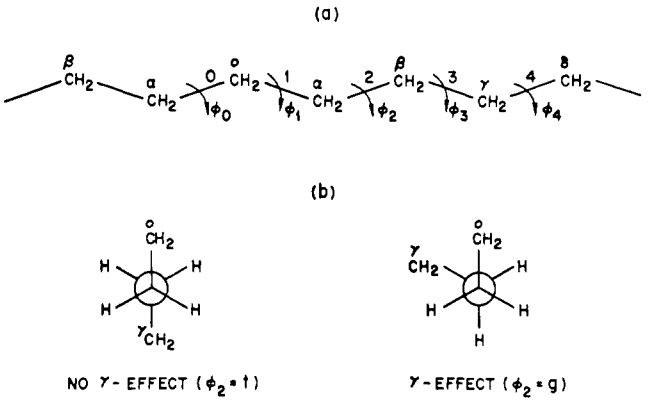

Figure 1. (a) Portion of a paraffinic hydrocarbon chain in the all-trans, planar zigzag conformation. (b) Newman projections along bond 2 in a illustrating the γ effect.

nuclei. The connection between vinyl polymer microstructure, conformation, and ^{13}C chemical shifts is provided by the conformationally sensitive γ-gauche effect.[1]

It has been observed[6-9] that when a carbon atom is proximal to a non-hydrogen γ substituent, which can occur if the intervening bond is in the gauche conformation (see Figure 1), then it is magnetically shielded and resonates upfield from carbons without γ substituents or those carbons that have γ substituents in the more distant trans arrangement. Consequently the populations of gauche and trans bonds in the vicinity of a carbon nucleus determine its relative chemical shift. Local polymer microstructure determines local polymer conformation and, through the conformationally sensitive γ-gauche effect, the ^{13}C NMR chemical shifts of its constituent carbon nuclei.

The γ-gauche effect method has been successfully applied[1] to calculate the ^{13}C NMR chemical shifts in a wide variety of vinyl homo- and copolymers. Polypropylene[10] and its oligomers[11,12] and copolymers with ethylene[13,14] and vinyl chloride,[15] poly(vinyl chloride) and its oligomers[16] and copolymers with ethylene,[17,18] propylene,[15] and methyl acrylate,[19] polystyrene[20] and its oligomers,[21] poly(propylene oxide),[22] and several fluoropolymers[23] have all been treated via the γ-gauche effect method to produce calculated ^{13}C NMR chemical shifts which reproduce the observed spectra and their dependences on stereosequence, comonomer sequence, and defect structures, such as head-to-head monomer additions. The calculated ^{13}C chemical shifts are valuable to the assignment of vinyl polymer ^{13}C NMR spectra and lead to a detailed microstructural description of these polymer chains. In addition, because the γ-gauche effect method of calculating ^{13}C NMR chemical shifts relies on a conformational description of the polymer to obtain gauche and trans bond populations, comparison of the calculated chemical shifts with the observed spectra serves to test the validity of the conformational model adopted for the polymer.

Ovenall[24] has recently reported the 100-MHz ^{13}C NMR spectra of isotactic and atactic poly(vinyl alcohol) (PVOH) in D_2O and dimethyl-d_6 sulfoxide (Me_2SO-d_6) solutions and analyzed the spectra for microstructural details. Also recently, Wolf and Suter[25] have derived a rotational isomeric states (RIS) treatment of PVOH conformational characteristics. These two developments permit us to calculate the ^{13}C chemical shifts expected for PVOH and to compare them with their observed spectra.

Calculation of ^{13}C NMR Chemical Shifts

Wolf and Suter[25] have calculated the conformational

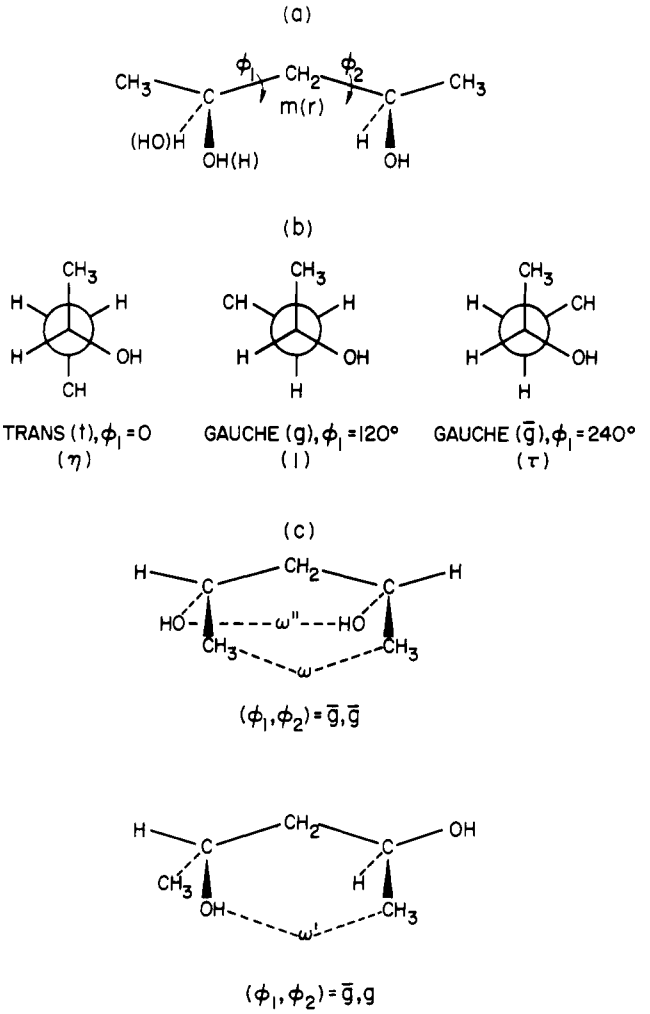

Figure 2. (a) m(r) isomer of 2,4-pentanediol in the (ϕ_1,ϕ_2) = 0°, 0° or t,t conformation. (b) Newman projections along bond 1 illustrating the first-order interactions η and τ dependent upon ϕ_1. (c) m 2,4-pentanediol in the $(\phi_1,\phi_2) = \bar{g},\bar{g}$ and $\bar{g},g$ conformations illustrating the second-order interactions ω, ω', and ω''.

energies of the PVOH "dimer" 2,4-pentanediol. They considered both the meso (m) and racemic (r) isomers and either ignored or included electrostatic interactions depending on whether or not the dimer was dissolved in H_2O or in apolar, aprotic solvents. Conformational energy maps were condensed into two PVOH intradiad matrices $\mathbf{U}_m''$ and $\mathbf{U}_r''$:

$$\mathbf{U}_m'' = \begin{array}{c|ccc} \phi_1/\phi_2 & t & g & \bar{g} \\ \hline t & \eta^2\omega'' & \eta & \eta\tau\omega' \\ g & \eta & \omega & \tau\omega' \\ \bar{g} & \eta\tau\omega' & \tau\omega' & \tau^2\omega\omega'' \end{array} \qquad (1)$$

$$\mathbf{U}_r'' = \begin{array}{c|ccc} \phi_1/\phi_2 & t & g & \bar{g} \\ \hline t & \eta^2 & \eta\omega' & \eta\tau\omega'' \\ g & \tau\omega' & 1 & \tau\omega \\ \bar{g} & \eta\tau\omega'' & \tau\omega & \tau^2\omega'^2 \end{array}$$

The elements of these matrices[26] are statistical weight parameters describing the interactions of nonbonded atoms. η and τ are first-order interactions between nonbonded atoms separated by three bonds and depend on only a single backbone rotation (see Figure 2a,b). ω,ω', and ω'' describe the second-order interactions dependent on neighboring pairs of backbone rotations between atoms separated by four bonds. As an example, the 3,2 element

Table I
Wolf-Suter[25] Statistical Weight Parameters, $\alpha = \alpha_0 \exp[-E_a/RT]$, for PVOH

	α_0			E_a[a]		
α	I[b]	II[c]	III[d]	I[b]	II[c]	III[d]
η	1.18	0.97	1.02	−0.39	−0.96	−0.76
τ	0.65	0.56	0.60	0.0	−0.27	−0.22
ω	1.34	1.30	1.13	1.83	1.81	1.56
ω'	1.03	0.90	1.03	0.85	0.79	0.84
ω''	0.87	0.68	1.05	0.32	1.01	1.04

[a] Energies are in kcal/mol. [b] Coulombic interactions ignored. [c] Coulombic interactions included; partial charges on "pseudoatoms" X. [d] Coulombic interactions included; partial charges on O.

of $\mathbf{U}_m''$ is the product $\tau\omega'$ and occurs because in the $\bar{g},g$ conformer there is a single first-order interaction corresponding to τ (see Figure 2b) and a single second-order interaction between CH_3 and OH (see Figure 2c). The values calculated for these statistical weight parameters by Wolf and Suter[25] are presented in Table I.

Three sets of statistical weight parameters are presented in Table I, because Wolf and Suter[25] applied three different methods to treat the Coulombic interactions in 2,4-pentanediol. The first approach, thought to be appropriate for H_2O and other polar, protic, strong hydrogen-bond-accepting solvents, completely ignores the electrostatic interactions. Coulombic interactions are considered in the other two methods, which differ only in the placement of partial charges, and are believed to be appropriate for aprotic solvents. Following Jorgensen,[27] the partial charge on O was equally distributed onto two pseudoatoms, X, representing the two lone-pair electron couples. In the other approach partial charges were placed on all of the atoms including O.

The RIS model obtained by ignoring Coulombic interactions reproduces the vicinal proton–proton coupling constants measured[28-30] by ^1H NMR for 2,4-pentanediol in H_2O and the dimensions of atactic PVOH also measured[31] in water. When the two RIS models derived for PVOH with inclusion of electrostatic interactions by Wolf and Suter[25] are modified to account for the formation of intramolecular hydrogen bonds in aprotic solvents (see Figure 2c), then the vicinal proton–proton couplings observed[29,30] for 2,4-pentanediol in the aprotic solvents pyridine, chloroform, and methylene chloride are also reproduced. This modification involves the addition of −1 kcal/mol to the energy of interaction between adjacent OH groups, $\mathbf{E}_{\omega''}$, which in aprotic solvents, unlike H_2O, can only form intramolecular hydrogen bonds.

In combination with the interdiad matrix $\mathbf{U}'$, $\mathbf{U}_m''$ and

$$\mathbf{U}' = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{vmatrix} \quad (2)$$

$\mathbf{U}_r''$ can be used to calculate[26] bond conformation probabilities for PVOH as a function of stereosequence. From these bond conformation probabilities the frequencies, $F\gamma$, of γ-gauche interactions between methine and methylene carbons and between methine carbons and OH groups are obtained.

The ^{13}C NMR chemical shifts are then calculated from

$$\delta_{CH_2} = F\gamma_{CH_2,CH}\gamma_{CH_2,CH} \quad (3)$$

$$\delta_{CH} = F\gamma_{CH,CH_2}\gamma_{CH,CH_2} + F\gamma_{CH,OH}\gamma_{CH,OH} \quad (4)$$

where $\gamma_{a,b}$ is the shielding in ppm produced at carbon a by γ substituent b when a and b are in a gauche arrangement. From our experience with other vinyl polymers[1,10-23] and by comparing the ^{13}C NMR chemical shifts[32] of aliphatic alcohols and the corresponding alkanes, we expect $\gamma_{CH_2,CH} \approx \gamma_{CH,CH_2} \simeq -5$ ppm and $\gamma_{CH,OH} \approx -7$ ppm. ^{13}C NMR chemical shifts were calculated for the methine carbons belonging to all possible pentad stereosequences and hexad stereosequences were considered for the methylene carbons.

Table II
^{13}C NMR Chemical Shifts Calculated for the Methylene Carbons in PVOH at the Hexad Stereosequence Level

	δ_{CH_2}, ppm		
hexad	I[a]	II[b]	III[b]
mrmrm	0.0	0.0	−0.09
rrmrm	−0.04	−0.02	−0.14
rrmrr	−0.07	−0.03	−0.18
mrrrm	−0.14	−0.04	−0.09
mrrrr	−0.19	−0.06	−0.12
rrrrr	−0.22	−0.07	−0.14
mmmrm	−0.45	−0.34	−0.08
rmmrm	−0.45	−0.32	−0.07
mmmrr	−0.49	−0.35	−0.11
rmmrr	−0.49	−0.33	−0.09
rmrrm	−0.62	−0.42	−0.09
mmrrm	−0.65	−0.43	−0.10
rmrrr	−0.66	−0.43	−0.12
mmrrr	−0.70	−0.44	−0.13
rmmmr	−0.81	−0.63	0.0
mmmmr	−0.84	−0.64	−0.01
mmmmm	−0.89	−0.66	−0.02
rmrmr	−1.09	−0.79	−0.09
mmrmr	−1.13	−0.81	−0.10
mmrmm	−1.19	−0.83	−0.10

[a] Using RIS model[25] appropriate to H_2O. [b] Using RIS models[25] applicable to aprotic solvents.

Table III
^{13}C NMR Chemical Shifts Calculated for the Methine Carbons in PVOH at the Pentad Stereosequence Level

	δ_{CH}, ppm		
pentad	I[a]	II[b]	III[b]
rmmr	0.0	0.0	0.0
mmmr	−0.07	−0.04	−0.05
mmmm	−0.17	−0.10	−0.11
rmrr	−0.43	−0.37	−0.61
rmrm	−0.48	−0.49	−0.68
mmrr	−0.50	−0.50	−0.66
mmrm	−0.57	−0.54	−0.74
rrrr	−0.76	−0.86	−1.20
mrrr	−0.81	−0.90	−1.28
mrrm	−0.88	−0.94	−1.36

[a] Using RIS model[25] appropriate to H_2O. [b] Using RIS models[25] applicable to aprotic solvents.

Results and Discussion

Tables II and III present the calculated ^{13}C NMR chemical shifts for the methylene carbons to the hexad level and for the methine carbons to the pentad level of PVOH stereosequence. All chemical shifts were calculated at 50 °C, the temperature employed by Ovenall[24] to record the ^{13}C NMR spectra of PVOH. In Figures 3 and 4 the ^{13}C chemical shifts observed for the methylene carbons in atactic PVOH dissolved in D_2O and Me_2SO-d_6, respectively, by Ovenall[24] are compared to those calculated by using the PVOH RIS models developed by Wolf and Suter.[25]

The sample of atactic PVOH studied by Ovenall[24] was found to have a Bernoullian stereosequence characterized by $P_m = 0.46$, i.e., 46% m diads and 54% r diads. Yet in D_2O the more intense trio of hexad resonances centered at 44.82 ppm was assigned to the rmr centered hexads while the less intense trio centered at 45.01 ppm was as-

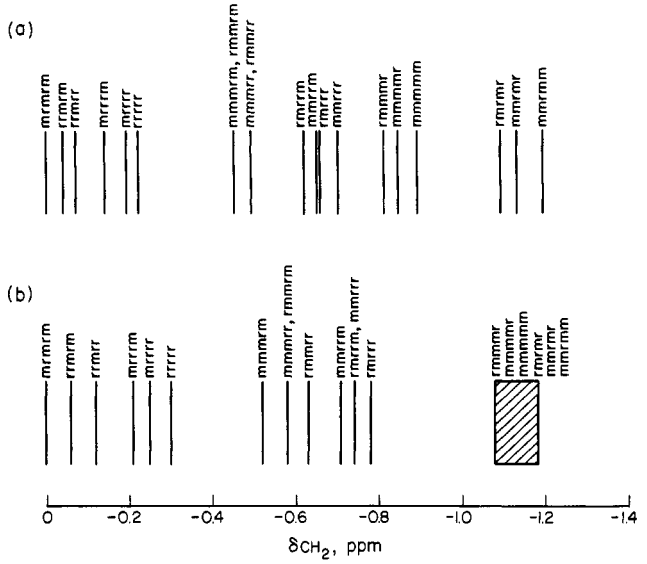

Figure 3. Comparison of ^{13}C chemical shifts in the form of stick spectra for the CH_2 carbons in atactic PVOH, where the calculated chemical shifts are given in a and those observed in D_2O by Ovenall[24] are presented in b.

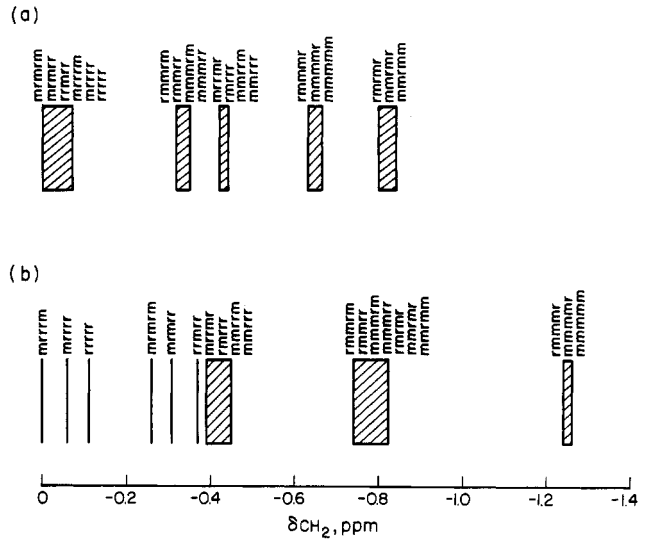

Figure 4. Same as Figure 3 except replace "D_2O" with Me_2SO-d_6.

signed to the rrr centered hexads by Ovenall.[24] Because the PVOH studied by Ovenall[24] is richer in r diads compared to m diads, a more consistent assignment of these two sets of resonances would be xrmry hexads centered at 45.01 ppm and xrrry hexads centered at 44.82 ppm. For the same reason, we believe a reversal in the assignments made by Ovenall[24] for the mrr and mmr centered hexad resonances is also reasonable. These modifications in the assignment of methylene carbon resonances in the ^{13}C NMR spectrum of atactic PVOH dissolved in D_2O have been incorporated in Figure 3b.

With the exception of a 0.1–0.2 ppm downfield shift of the resonances calculated for mmm centered methylene carbon hexads compared to the observed resonances, there is excellent agreement between the methylene ^{13}C chemical shifts calculated and observed for atactic PVOH in D_2O. Both the observed order of resonances and the overall dispersion in methylene carbon chemical shifts are closely reproduced by the calculated chemical shifts. This agreement lends support to Wolf and Suter's[25] RIS model for PVOH dissolved in H_2O (I) and suggests that the shielding of a methylene carbon nucleus by a methine carbon in PVOH is similar ($\gamma_{CH_2,CH}$ = −5 ppm) to that experienced by the methylene carbons in other vinyl polymers.[1,10–23]

Methine carbon resonances observed for PVOH in D_2O solution follow the same order as the chemical shifts calculated for the methine carbons which are presented in Table III. However, while the calculated overall dispersion is ~1 ppm, the observed methine resonances span a ~3 ppm range. For the methine carbon resonances observed by Ovenall[24] in Me_2SO-d_6 the order of resonances is the same as that calculated for the methine carbons in aprotic solvents using the Wolf–Suter[25] RIS models for PVOH (II and III) (see Table III), which account for intramolecular electrostatic and hydrogen-bonding interactions. Again the calculated dispersion in methine carbon chemical shifts 1–1.4 ppm is greatly exceeded by the observed range of 4 ppm.

In Figure 4 we compare the methylene carbon chemical shifts observed for PVOH in Me_2SO-d_6 by Ovenall[24] to those calculated by using the PVOH RIS model II of Wolf and Suter.[25] We do not plot the methylene carbon chemical shifts calculated with RIS model III, because all 20 hexad resonances fell within the narrow range of less than 0.2 ppm. Clearly the agreement between the chemical shifts calculated and observed for the methylene carbons in Me_2SO-d_6 is not as good as that found in D_2O (compare Figures 3 and 4). The order of the methylene chemical shifts calculated for D_2O (I) and Me_2SO-d_6 (II) are the same, but there is a 30% reduction in the overall spread of methylene carbon chemical shifts calculated for Me_2SO-d_6 compared to those calculated for D_2O as solvent.

Experimentally, on the other hand, the overall observed spreads in the methylene carbon chemical shifts are nearly identical for D_2O and Me_2SO-d_6. Changing solvent from D_2O to Me_2SO-d_6 causes the rrr centered hexad resonances to move downfield from those of the rmr centered hexads, the mrr centered hexads to resonate downfield from the mmr centered hexads, and the mrm and mmr centered hexad resonances to overlap. Substitution of Me_2SO-d_6 for D_2O as solvent results in a downfield shift of resonances belonging to the rrr, mrr, and mrm centered hexads, an upfield shift of rmr and mmr centered hexad resonances, and no change for the mmm centered hexad resonances.

We concur with Ovenall,[24] who attributed the changes observed in the ^{13}C NMR spectra of atactic PVOH with solvent to differences in the average polymer chain conformation in the solvents D_2O and Me_2SO-d_6. The RIS models for PVOH in D_2O (I) and Me_2SO-d_6 (II) derived by Wolf and Suter[25] do predict different average conformations for PVOH in these solvents. They do not, however, predict the observed crossover among several methylene carbon residues when changing solvent from D_2O to Me_2SO-d_6.

Irrespective of stereosequence, the fraction of gauche bonds, which is directly related to the calculated δ_{CH_2}'s (see eq 3), is found to be higher for PVOH in D_2O compared to Me_2SO-d_6 as solvent. In fact, for all methylene carbon hexads the calculated frequency of γ-gauche interactions between the methylene and methine carbons ($F\gamma_{CH_2,CH}$, see eq 3) is 0.2 less in Me_2SO-d_6 than in D_2O. This explains the contraction in the overall spread of calculated methylene carbon chemical shifts when passing from D_2O to Me_2SO-d_6 (see Figures 3a and 4a), and also accounts for the experimentally observed upfield shift of 1 ppm [$(\Delta F\gamma_{CH_2,CH})(\gamma_{CH_2,CH})$ = (0.2)(−5 ppm) = −1 ppm] for the entire methylene carbon region when passing from Me_2SO-d_6 to D_2O.

Obviously for the methine pentads $F\gamma_{CH,CH_2}(D_2O)$ is 0.2 > $F\gamma_{CH,CH_2}(Me_2SO$-$d_6)$. In addition $F\gamma_{CH,OH}(D_2O)$ is 0.2

$< F\gamma_{CH,OH}(Me_2SO\text{-}d_6)$, resulting in calculated methine carbon chemical shifts which are nearly independent of solvent. This solvent independence of the average location of the PVOH methine carbon region is also observed in the ^{13}C NMR spectra recorded for atactic PVOH by Ovenall.[24]

The following expressions describe the calculated overall spreads in methine carbon pentad ^{13}C chemical shifts; in D_2O (I) $\Delta\delta_{CH,OH} = 0.28\gamma_{CH,OH}-0.21\gamma_{CH,CH_2}$ and in $Me_2SO\text{-}d_6$ (II) $\Delta\delta_{CH} = 0.25\gamma_{CH,OH}-0.16\gamma_{CH,CH_2}$. In order to match the observed spreads (3 and 4 ppm), $\gamma_{CH,OH}$ must be at least −15 ppm. There is no indication from the ^{13}C NMR spectra[32] of alkanes and aliphatic alcohols that the shielding produced at a carbon nucleus by a γ-gauche OH group can attain this magnitude. We therefore conclude that in addition to γ-gauche shielding effects, the ^{13}C chemical shifts of the carbon nuclei in PVOH are affected by some additional mechanism, especially the methine carbons.

An obvious candidate would appear to be hydrogen bonding. When a methine carbon in PVOH is gauche to its γ OH group, it becomes possible to form a hydrogen bond between its own OH and the OH in the γ position. This hydrogen bond would likely affect the methine carbon chemical shift, and might produce a significant shielding over and above that resulting from the gauche arrangement of its γ OH, leading to an apparently larger $\gamma_{CH,OH}$. Whether or not this mechanism is feasible, it still remains to explain the observed crossover of several methylene carbon resonances when changing solvent from D_2O to $Me_2SO\text{-}d_6$.

Our analysis of the ^{13}C NMR spectra of atactic PVOH recorded in D_2O and $Me_2SO\text{-}d_6$ by Ovenall[24] using the γ-gauche effect method of calculating ^{13}C chemical shifts lends support to the RIS models developed for PVOH by Wolf and Suter.[25] Model I, which ignores electrostatic interactions, appears to be appropriate to PVOH dissolved in D_2O. Modeling the electrostatic interactions after the method of Jorgensen,[27] where partial charges are assigned to pseudoatoms at the positions of the lone electron pairs on the oxygen atom, and attributing a 1 kcal/mol stabilization for second-order OH—OH interaction (ω'') (see Figure 2c) leads to model II, which seems to adequately describe the conformations of PVOH in aprotic solvents like $Me_2SO\text{-}d_6$. On the basis of the near independence of methylene carbon chemical shifts to PVOH stereosequence when calculated with model III, we conclude that treating the electrostatic interactions by placing the partial charge for O directly on the oxygen atoms is not appropriate.

The differences in the ^{13}C NMR spectra of atactic PVOH when changing solvent from D_2O to $Me_2SO\text{-}d_6$ observed by Ovenall[24] are attributable to differences in the average PVOH chain conformations in these solvents. It appears that the Wolf–Suter RIS models I and II satisfactorily account for the average PVOH conformations in D_2O and $Me_2SO\text{-}d_6$, respectively. These conclusions were permitted by comparing the ^{13}C chemical shifts calculated with the γ-gauche effect method[1] to the observed ^{13}C NMR spectra of PVOH, and serve to demonstrate the utility of the method in the study of vinyl polymer microstructures and conformational characteristics.

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