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Failure of the γ-Gauche Effect Method To Predict the Stereosequence-Dependent ^{13}C NMR Spectrum of the Disubstituted Vinyl Polymer Atactic Poly(methyl methacrylate)

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ABSTRACT: The conformationally sensitive γ-gauche effect has been successfully employed to make and/or rationalize the assignment of resonances observed in the ^{13}C NMR spectra of vinyl homo- and copolymers recorded in solution. When a carbon nucleus is in a gauche arrangement with a nonprotonic, γ-substituent three bonds removed, its ^{13}C resonance frequency is shifted upfield, or it is shielded, by ca. 5 ppm compared to their trans arrangement. Because the local populations of trans and gauche bond conformers depend sensitively on local stereosequence, the ^{13}C NMR spectra of vinyl polymers usually exhibit a marked dependence on their stereochemical microstructures. Knowledge of vinyl polymer conformational characteristics, from which the trans and gauche bond conformer populations can be obtained for all possible local stereosequences, permits an estimate of their stereosequence-dependent ^{13}C chemical shifts via the γ-gauche effect method. This approach has proved successful for assigning the ^{13}C NMR spectra, and thereby determining the stereosequences, of many vinyl polymers. Here we apply the γ-gauche effect method to atactic poly(methyl methacrylate) (PMMA) and find it to fail in the prediction of stereosequence-dependent ^{13}C NMR chemical shifts, even though the ^{13}C NMR spectra of the structurally similar monosubstituted vinyl polymers poly(methyl acrylate) and poly(vinyl acetate) can be reproduced by the γ-gauche effect method. Sensitivity of the backbone valence angles at the quaternary carbons to the conformations of the adjoining bonds is suggested as a likely source for the failure of the γ-gauche effect method when applied to the ^{13}C NMR spectra of sterically crowded, disubstituted vinyl polymers like PMMA.

Introduction

Recently, Schneider et al.[1,2] have reported the high-resolution, solid-state ^{13}C NMR spectra of crystalline isotactic (i), crystalline syndiotactic (s), and the crystalline i*s (1:1.5) complex (c) of poly(methyl methacrylate) (PMMA). The PMMA chains adopt[3,4] a nearly all-trans conformation whether crystallized in their separate pure phases (i or s) or in their stereocomplex (c) form. The most striking features of the CPMAS/DD ^{13}C NMR spectra reported by Schneider et al.[1,2] were the ca. 6–10 ppm chemical shift differences observed for the α-CH$_3$ resonances in the crystals of i-, s-, and c(i*s)-PMMA, which are summarized in Table I.

Table I
^{13}C Chemical Shifts of α-CH$_3$ Resonances Observed[1,2] in Stereoregular, Crystalline PMMAs

PMMA	δ(α-CH$_3$), ppm from TMS
i	23.7
s	15.25, 17.7
c(i*s)	24.4(i), 14.85(s)

Why do the α-CH$_3$ carbons in i- and s-PMMA resonate at frequencies separated by 6–10 ppm when crystallized in their pure phases or as their stereocomplex even though the local conformations of both stereoregular, crystalline PMMA's are nearly all-trans?

It has been amply demonstrated,[5,6] in both the solution and solid states, that the stereosequence-dependent ^{13}C NMR chemical shifts observed for vinyl polymers have as their principle origin the stereosequence dependence of the local conformation in the vicinity of each resonating ^{13}C nucleus. The γ-gauche effect[5,6] has been utilized to make the conformational connection between vinyl polymer stereosequence and ^{13}C NMR spectra. When an observed carbon, C$^{\circ}$, and its nonprotonic γ-substituent (S$^{\gamma}$), which are separated by three intervening bonds, are in a gauche arrangement, or conformation, C$^{\circ}$ is observed to resonate several ppm upfield from their more distant arrangement in the trans conformation. For $S^{\gamma} = C^{\gamma}$, the shielding produced at C$^{\circ}$ by their gauche arrangement is generally ca. 5 ppm.

By constrast to the intramolecular, conformational influence (γ-gauche effect) on vinyl polymer ^{13}C chemical shifts, the intermolecular effects on δ ^{13}C produced by different packing arrangements, particularly in the solid state, are usually much smaller[6] (1–2 ppm). Thus, it seems difficult to understand why the α-CH$_3$ carbons in s-PPMA resonate 6–10 ppm upfield from their counterparts in i-PMMA when they are crystallized in separate or complex forms, because both the i- and s-PMMA chains are adopting very similar, nearly all-trans backbone bond conformations.

Schneider et al.[1,2] suggest that the relative orientations of the α-CH$_3$ and ester groups bonded to the same quaternary carbon are different in i- and s-PMMA when crystallized, and it is this difference in the conformation about the –C—C(=O)– side chain bond that produces such a large difference in the observed α-CH$_3$ chemical shifts (see Table I).

Vacatello and Flory[7] concluded that the lowest energy arrangements of α-CH$_3$ and ester groups place either the carbonyl oxygen (C=O) or the ester oxygen (C—O) in a cis arrangement with α-CH$_3$. Even if, for example, all the carbonyl oxygens were cis to the α-CH$_3$ groups in i-PMMA, while all the ester oxygens in s-PMMA were cis to their α-CH$_3$'s, it is difficult to understand how the cis arrangements of carbonyl or ester oxygens could produce such substantial chemical shift differences (6–10 ppm), because in both instances the α-CH$_3$ carbon is cis to a γ-oxygen.

Vacatello and Flory[7] found the valence angle τ at the quaternary carbon ($\angle$CH$_2$–C–CH$_2$) to depend on the conformations of the adjacent backbone bonds: $\tau = 106°$ when both adjacent bonds are trans, $\tau = 111°$ when one is trans and the other gauche, and $\tau = 116°$ when both are gauche. On the other hand, $\tau' = \angle$ –C–CH$_2$–C– was found to be 124 ± 1° independent of the backbone conformation of PMMA. We might except the resonance frequency of

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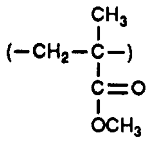
α-CH_3 to be sensitive to the backbone valence angle at $-C-(\tau)$ to which it is attached. However, both the i- and s-PMMA chains adopt the nearly all-trans backbone conformation in their crystals and should have similar τ angles.

In an attempt to learn the source of the disparity between the chemical shifts observed[1,2] for the α-CH_3 carbons in crystalline i- and s-PMMA, we have used the Vacatello and Flory[7] conformational description of PMMA to calculate the ^{13}C chemical shifts of all the carbons in i- and s-PMMA averaged over all of their low-energy conformations. This was accomplished via the γ-gauche effect method.[5,6] ^{13}C chemical shifts calculated for i- and s-PMMA were then compared to the ^{13}C NMR spectrum of atactic (a)-PMMA recorded in solution. In addition, the γ-gauche effect method of calculating stereosequence-dependent ^{13}C chemical shifts was also applied to the monosubstituted vinyl polymers poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc) whose ester group side chains are very similar to those of PMMA. ^{13}C chemical shifts calculated for PMA and PVAc were compared to the ^{13}C NMR spectra of a-PMMA and a-PVAc observed in solution.

Comparison of the stereosequence-dependent ^{13}C chemical shifts calculated via the γ-gauche effect method in the ^{13}C NMR spectra recorded in solution for a-PMMA, a-PMA, and a-PVAc will permit us to determine whether or not ^{13}C NMR spectroscopy accurately reflects the local bond conformations of these vinyl polymers when rapidly averaging over their low-energy conformations in solution. If we are unable to predict the ^{13}C chemical shifts observed in their solutions, then conformational analyses of their solid-state ^{13}C NMR spectra, such as those reported by Schneider et al.[1,2] for crystalline i- and s-PMMA, must be approached with caution.

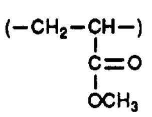
Calculation of ^{13}C NMR Chemical Shifts

The γ-gauche effect method for calculating the ^{13}C NMR chemical shift of vinyl polymers, as detailed in refs 5 and 6, requires two types of information: the degree to which a γ-substituent (S^γ) shields a carbon nucleus in the polymer when they are in a gauche arrangement and the conformational characteristics of the polymer which enables us to estimate the frequency of such γ-gauche arrangements. For PMMA, PMA, and PVAc



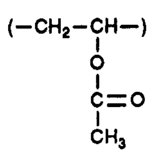
$(-CH_2-C(CH_3)(C(=O)OCH_3)-)$

PMMA



$(-CH_2-CH(C(=O)OCH_3)-)$

PMA



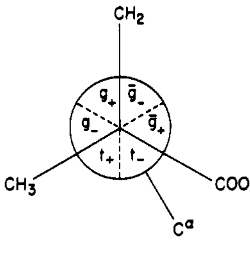
$(-CH_2-CH(O-C(=O)-CH_3)-)$

PVAc

we need only specify $\gamma_{C,C}$ and $\gamma_{C,O}$, the shieldings produced by S^γ = C and O when in a gauche arrangement with the observed carbon atom C^o.

From past experience,[5,6] we know that $\gamma_{C,C} = -2$ to -6 ppm, and a comparison of the methyl carbon chemical shifts observed[8] for *n*-butane an *n*-propyl alcohol leads to $\gamma_{C,O} = -5$ to -7 ppm. The rotational isomeric state (RIS) models developed by Vacatello and Flory[7] for PMMA, by Yoon et al.[9] for PMA, and by Sundararajan[10] for PVAc were employed to calculate[11] the stereosequence-dependent bond conformational populations for these vinyl polymers to obtain the frequencies of γ-gauche carbon atom arrangements in each.

The six-state RIS model developed by Vacatello and Flory[7] for PMMA is illustrated in Figure 1. For the t_-, t_+, g_-, g_+, $\bar{g}_-$, and $\bar{g}_+$ rotational states, the dihedral angles between the quaternary (C^α) and methylene (CH_2) carbons are 160, 170, 80, 55, 55, and 80°, respectively. On the basis of our experience[12] with dihedral angle dependent γ-effects, we assign $\gamma_{C,C} = 0, 0, -2.5, -5, -5$, and -2.5 ppm shieldings to these conformations. Dihedral angles of 80, 50, 40, 65, 175, and 160° between α-CH_3 and C^α in the t_-, t_+, g_-, g_+, $\bar{g}_-$, and $\bar{g}_+$ rotational states were assigned $\gamma_{C,C} = -2.5, -5.5, -6, -5, 0$, and 0 ppm, while $\gamma_{C,C} = -6, -4.5, 0, 0, -5$, and -6 ppm were adopted for the shieldings resulting from 40, 70, 160, 175, 65, and 40° dihedral angles between C^α and C=O.



$\phi = -20°(t_-), 10°(t_+), 100°(g_-),$
$125°(g_+), -125°(\bar{g}_-)$, and $-100°(\bar{g}_+)$.

Figure 1. Schematic diagram illustrating the six-state RIS model for PMMA derived by Vacatello and Flory.[7]

Table II
Comparison of Observed[13] and Calculated ^{13}C NMR Chemical Shifts for a-PMMA in Solution

	δ ^{13}C, ppm	
carbon	obsd	calcd
C^α	$\Delta\delta = 1.0$ (mm, mr, rr)[a]	$\Delta\delta = 0$
CH_2	$\Delta\delta = 2.5$ (r, m)	$\Delta\delta = 1.3$ (r, m)
CH_3	$\Delta\delta = 5.3$ (mm, mr, rr)	$\Delta\delta = 1.4$ (mm, mr, rr)
C=O	$\Delta\delta = 2.0$ (rr, mr, mm)	$\Delta\delta = 0.9$ (mm, mr, rr)

[a] Order of stereosequence-dependent resonances from low to high field.

The RIS model[9] for PMA restricts the backbone bonds to two rotational states, trans (t) and gauche (g) (see Figure 1, where CH_3 is replaced by H in PMA). In the t state, C^α and C=O are gauche, while in the g state C^α and CH_2 are gauche. Both gauche arrangements were assumed to shield the carbon nuclei by $\gamma_{C,C} = -5$ ppm.

Sundararajan's[10] RIS model for PVAc is a three rotational state description, one trans (t) and two gauche (g and $\bar{g}$) states. (Note for PVAc the CH_3 and C(=O)—O—CH_3 groups of Figure 1 are replaced by H and O—C(=O)—CH_3, respectively.) For the gauche arrangements of CH_2, C^α and C^α, O, $\gamma_{C,C} = -5$ and $\gamma_{C,O} = -7$ ppm were assumed.

Matrix multiplication methods[11] were used to calculate the probabilities that each of the backbone bonds adopts either of the trans (t, t_-, t_+) or gauche (g, $\bar{g}$, g_-, g_+, $\bar{g}_-$, $\bar{g}_+$) rotational states. For each polymer, stereosequences to the pentad level were considered for the C^α, α-CH_3, and C=O carbons, while all tetrad stereosequences were considered in the calculations of ^{13}C chemical shifts for the CH_2 carbons.

Results and Discussion

PMMA. In Table II, the ^{13}C chemical shifts calculated for PMMA via the γ-gauche effect method are compared to the observed chemical shifts reported by Peat and Reynolds[13] for an a-PMMA recorded in $CDCl_3$ at 32 °C. It is clear that the conformationally sensitive γ-gauche effect method of calculating ^{13}C chemical shifts simply does not reproduce the stereosequence-dependent ^{13}C chemical shifts observed for a-PMMA. Significant discrepancies are apparent between the observed and calculated overall, stereosequence-dependent spreads in ^{13}C chemical shifts ($\Delta\delta$) for all four carbon types. In addition, the observed order of triad stereosequence resonances for the C=O carbon is rr, mr (rm), mm (from low to high field), while the calculated order is reversed, mm, mr (rm), rr.

PMA. In the ^{13}C NMR spectrum of a-PMA recorded in *o*-dichlorobenzene at 140 °C by Matsuzaki et al.,[14] only the CH_2 and C=O carbon resonances show a slight stereosequence dependence characterized by $\Delta\delta = 1.0$ (CH) and 0.2 (C=O) ppm. The order of CH_2 tetrad stereosequence resonances was given as rmr + rrr, mmr + mrr, mrm + mmm from low to high field. Though not shown, this order of stereosequence resonances agrees qualitatively with the ^{13}C chemical shifts calculated here for the methylene carbons. ^{13}C chemical shifts calculated to the pentad stereosequence level for the C^{α} carbons yielded an overall spread of C^{α} chemical shifts < 0.1 ppm in agreement with the single C^{α} resonance observed by Matsuzaki et al.[14] In addition, the calculated dispersion of C=O chemical shifts was similarly small and consistent with the observed $\Delta\delta(C{=}O) < 0.2$ ppm. In general, the relative insensitivity of the observed ^{13}C NMR spectrum of a-PMA to stereosequence is well reproduced by the ^{13}C chemical shifts estimated via the γ-gauche effect method.

PVAc. The 62.86-MHz ^{13}C NMR spectrum of a-PVAc recorded in $CDCl_3$ solution at 50 °C by Sung and Noggle[15] is presented in Figure 2. Below the methylene and methine carbon regions of the a-PVAc spectrum are presented the γ-gauche effect calculated chemical shifts in the form of stick spectra. Note the general agreement between observed and calculated chemical shifts for both carbon types. The observed overall spreads in CH_2 and CH resonances due to a-PVAc stereosequences are well reproduced by the calculated chemical shifts. Minor discrepancies between the experimental assignments of resonances and the calculated order of stereosequence-dependent CH_2 and CH chemical shifts may in part be a result of ambiguities in the experimental assignment as discussed by Sung and Noggle.[15]

To summarize then, the solution ^{13}C NMR spectra of a-PMA and a-PVAc can be faithfully reproduced by the conformationally sensitive γ-gauche effect method[5,6] of estimating ^{13}C chemical shifts. The relative sensitivity (independence) of the a-PVAc (a-PMA) spectrum to stereosequence is matched by the calculated chemical shifts. On the other hand, for the disubstituted vinyl polymer a-PMMA, the observed and estimated ^{13}C chemical shifts are in complete disagreement.

We believe that the most likely reason the stereosequence-dependent ^{13}C NMR spectrum of a-PMMA recorded in solution cannot be rationalized by the calculation of ^{13}C chemical shifts using the conformationally sensitive γ-gauche effect method[5,6] can be attributed to the conformational, and therefore configurational, sensitivity of the backbone and side chain geometry in this sterically crowded vinyl polymer. Vacatello and Flory[7] suggest that the backbone valence angle ∠C–CH_2–C– is expanded some 15° from the normal tetahedral value in order to reduce the repulsive interactions between side chain substituents and backbone atoms separated by four bonds, which occur for all possible pairs of adjacent backbone conformers. A single-crystal X-ray diffraction study[16] of the polyisobutylene (PIB) model compound 2,2,4,4-tetramethyladipic acid confirms the expansion of the ∠C–CH_2–C– valence angle suggested by Vacatello and Flory.[7] In the PIB model compound ∠C–CH_2–C– was found[16] to be 122.6°.

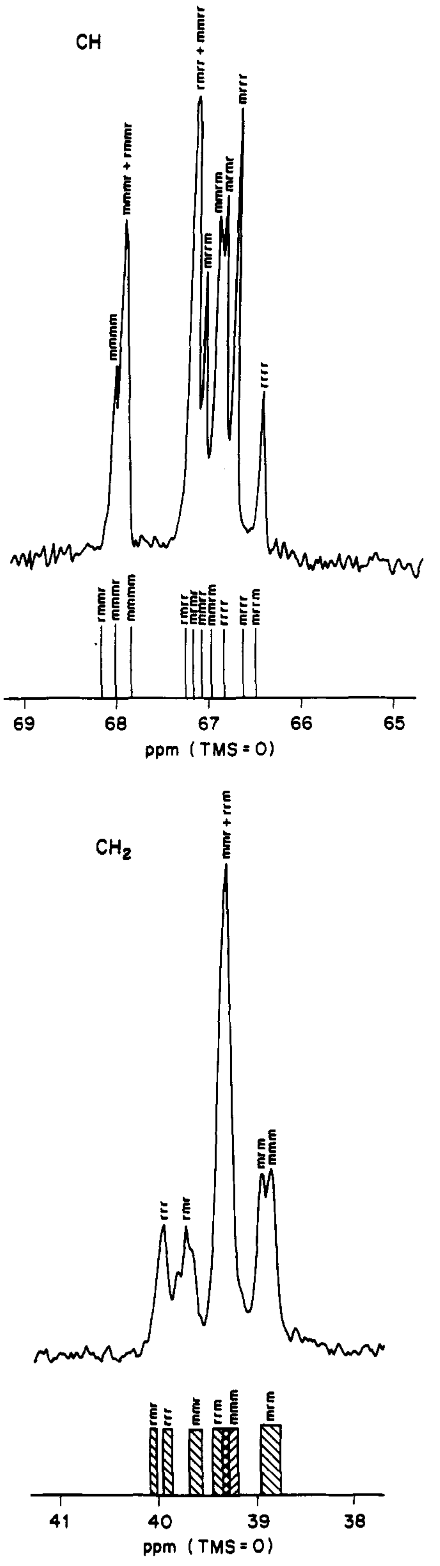


Figure 2. Comparison of the observed[15] 62.86-MHz ^{13}C NMR spectrum of a-PVAc recorded in $CDCl_3$ at 50 °C with the ^{13}C stick spectra of the CH and CH_2 carbons calculated via the γ-gauche effect method.[5,6]

The backbone valence angle at the quaternary carbon in PMMA was suggested by Vacatello and Flory[7] to depend on the conformations of the attached backbone bonds, with ∠CH_2–C–CH_2 = 106, 111, and 116° when both attached backbone bonds are trans, when one is trans and the other is gauche, and when both are gauche, respectively. This conformational dependence of PMMA backbone geometry is not considered when estimating ^{13}C chemical shifts via the γ-gauche effect method,[5,6] and probably accounts for the disparity between the estimated ^{13}C chemical shifts and the observed[13] ^{13}C NMR spectrum of a-PMMA. Clearly a variation of 10° in the CH_2–C–CH_2 valence angle produced by the stereosequence-dependent conformations of the attached backbone bonds might be expected to significantly influence the ^{13}C chemical shifts of a-PMMA over and above the shielding produced by the gauche arrangements of these same carbons and their γ-substituents. It would therefore appear that the γ-gauche effect method[5,6] of estimating the ^{13}C chemical shifts expected for disubstituted vinyl polymers may be inadequate, even though it may be successfully applied to the sterically less crowded monosubstituted vinyl polymers like PMA and PMAc.

Our failure to estimate the stereosequence-dependent ^{13}C NMR spectrum of a-PMMA observed in solution should serve as a caution when attempting to interpret the ^{13}C NMR spectra observed for solid PMMA's in terms of their solid-state conformations. Schneider et al.[1,2] have observed and isolated the solid-state ^{13}C NMR spectra of crystalline i-PPMA, s-PPMA, and the i*s (1:1.5) complex of PMMA. Though the i-PMMA and s-PMMA chains in their isolated and stereocomplexed crystalline phases adopt nearly the same approximately all-trans backbone conformation,[3,4] the chemical shifts of the methylene and α-CH_3 carbon (see Table I) resonances differ by 3–5 and 6–10 ppm, respectively, between the i- and s-PMMA chains.

These large ^{13}C chemical shift differences do not appear to arise from conformational differences, so we suggest that differences in the packing arrangements of i- and s-PMMA chains in their isolated and stereocomplexed crystals, which may lead to different CH_2–C–CH_2 valence angles, might account for the large shifts between the i- and s-PMMA CH_2 and α-CH_3 resonances. As a consequence, it would appear prudent to approach the conformational analysis of solid PMMA's via ^{13}C NMR spectroscopy with caution.

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