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# Comment on the Analysis of Vicinal Proton-Proton Coupling Constants in Polypropylene Chains

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In a recent paper Brückner et al.[1] calculated the vicinal proton-proton NMR coupling constants $J_{01}(H_0 \cdots H_1)$ and $J_{02}(H_0 \cdots H_2)$ in isotactic and syndiotactic polypropylenes. They found that by properly modifying the statistical treatment of unperturbed polypropylene chains previously devised by two of them,[2] it was possible to obtain values of the coupling constants in satisfactory agreement with those observed by Zambelli, Giongo, and Natta.[3]

In previous work done in this laboratory[4-6] and by Tonelli[7,8] it was shown that the $^{13}C$ NMR chemical shifts of polypropylene and of its model compounds can be accurately calculated by means of the five-state statistical model of the polypropylene chain.[9,10] Since any proposed model should behave properly with regard to as many as possible experimental data, it seemed to us important to verify whether the rotational isomeric state populations computed in our analysis of the $^{13}C$ chemical shifts would also account for the vicinal proton coupling constants. As quoted in ref 1, unpublished calculations by Tonelli based on the statistical model of Suter and Flory[10] appear to produce good agreement with the observed coupling constants.

Brückner et al.[1] assumed various forms of the Karplus equation to express the dependence of the coupling constants $J_{0k}$ ($k = 1, 2$) on the dihedral angle $H_0$-C-C-$H_k$. The absolute values of $J_{0k}$ computed by Brückner et al. for the two polymers depend considerably on the parameters utilized in the Karplus equation, but the differences $J_{01} - J_{02}$ are much less sensitive to the parameter set. The computed differences are in reasonable agreement with experiment, although they are constantly smaller than the observed values,[3] particularly in the case of syndiotactic polypropylene.

Recently, an empirical generalization of the Karplus equation has been proposed by Haasnoot, de Leeuw, and Altona,[11] who take into account electronegativity effects of the substituents on the HCCH fragment. Since the relationship proposed by these authors appears to be the most precise one currently available, we choose it for our calculations of the polypropylene coupling constants. For comparison we shall also present results obtained by using the Karplus equation with parameters derived from the analysis of 1,3,5,7-tetramethylcyclooctane stereoisomers:[12] such a parameter set provided the best results in Brückner et al.'s calculations.[1]

We computed the coupling constants $J_{0k}$ as Boltzmann averages over a discrete number of states, in the frame of the rotational isomeric state theory. The RIS populations were calculated exactly as for the analysis of the $^{13}C$ chemical shifts,[5,6] however here assuming infinite isotactic and syndiotactic polypropylene chains. Both models considered in ref 5 were utilized for the present calculations. The first one, denoted here as model A, was derived from Boyd and Breitling's model:[9] see ref 4 and 5 for the definition of the statistical weights. The second model (B) is that proposed by Suter and Flory.[10] In our previous application of these methods[5] the precise definition of the rotational states in terms of the dihedral angles C-C-C-C was unnecessary, due to lack of an accurate relationship between $^{13}C$ chemical shifts and angles. Thus the two models, from our point of view, differed only with regard to the statistical weight matrices. Here, in order to apply the equation given by Haasnoot et al.[11] (or the Karplus equation), we must associate values of the two dihedral angles $H_0$-C-C-$H_k$ ($\phi_k$) to each rotational isomeric state of a given bond of the chain (see Figure 1).

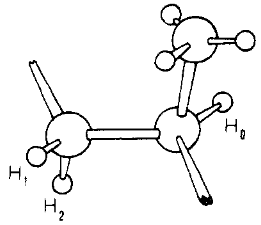

**Figure 1.**

As neither Boyd and Breitling[9] nor Suter and Flory[10] published the values of the HCCH angles corresponding to the five states of the main chain, we resorted to two criteria, which approximately take into account the works of these authors. One set of dihedral angles, indicated as model I, was taken as the weighted average, for each state, of the dihedral angles $\phi_k$ in conformations of minimum energy previously computed for the model compound 2,4,6-trimethylheptane.[5] A second model accounts for a major improvement of Suter and Flory's method over the work of Boyd and Breitling, namely, the replacement of energy minima with weighted averages representing conformational domains: due to the asymmetry of the nonbonded interactions involved, the average conformations are shifted significantly from the positions of minimum energy toward less staggered arrangements.[10] Thus in model II the values of $\phi_k$ were all corrected (except for one state) by an equal amount $\Delta\phi$: from inspection of the differences between the angles C-C-C-C in Suter and Flory's model[10] and the values computed by us for the minima, a value of $\Delta\phi = 7°$ was estimated. Since a different method was utilized to compute the hydrogen positions in the data file to which the parameters of Haasnoot et al.'s equation were fitted, and due to the errors affecting the hydrogen positions computed with any current molecular mechanics method,[11] perhaps $\Delta\phi$ should rather be considered as an adjustable parameter. We point out that changes of $\Delta\phi$ by a few degrees would affect the calculated $J_{0k}$ by a few tenths of a hertz, with very small effects on their relative values.

Following the notation of Haasnoot et al.,[11] the two coupling constants $J_{0k}$ can be expressed in the form $J_{01} = J_{CC/CH}(-\phi_1)$, $J_{02} = J_{CC/CH}(\phi_2)$. The values of $-\phi_1$ and $\phi_2$ corresponding to models I and II, together with the RIS populations obtained using statistical weights A and B, are listed in Table I. The coupling constants computed according to various models are reported in Table II. The results presented, by comparison with the experimental data, lead to the following conclusions.

(i) Model I overestimates all coupling constants, independently of the statistical weights and of the equation being used.

(ii) Model II yields values of $J_{0k}$ in good agreement with experiment, supporting the analysis of Suter and Flory[10] with regard to the geometrical definition of the five rotational isomeric states. The set II of dihedral angles given in Table I could then be utilized (in connection with Haasnoot et al.'s equation[11]) for predicting the vicinal proton coupling constants of the fragment $-CH_2CH(CH_3)-$ in other polymer chains.

(iii) As far as statistical weight matrices are concerned, models A and B give very close results for the syndiotactic

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Table I
Dihedral Angles (Deg) $H_0$-C-C-$H_k$[a] in Five-State Models of Polypropylene and RIS Populations Computed at 140 °C for Infinite Isotactic and Syndiotactic Chains

| state[b] | dihedral angles | | | | populations | | | |
|---|---|---|---|---|---|---|---|---|
| | model I | | model II | | model A[c] | | model B[d] | |
| | $-\phi_1$ | $\phi_2$ | $-\phi_1$ | $\phi_2$ | isotactic | syndiotactic | isotactic | syndiotactic |
| t | 180 | 65 | 173 | 72 | 0.4502 | 0.6121 | 0.4469 | 0.6034 |
| t* | 145 | 100 | 138 | 107 | 0.0825 | 0.0435 | 0.1369 | 0.0643 |
| g* | 100 | 145 | 107 | 138 | 0.0525 | 0.0439 | 0.0277 | 0.0533 |
| g | 65 | 180 | 72 | 173 | 0.3733 | 0.2669 | 0.3532 | 0.2514 |
| $\bar{g}$ | −56 | −56 | −56 | −56 | 0.0415 | 0.0336 | 0.0353 | 0.0276 |

[a] Positive clockwise rotations, with $\phi_k = 0°$ for the cis conformation, referred to Figure 1. [b] Defined for the main-chain carbon atoms, using Suter and Flory's notation.[10] [c] Reference 5. [d] Following ref 10.

Table II
Observed and Calculated Vicinal Proton Coupling Constants[a] in Isotactic and Syndiotactic Polypropylene

| | | isotactic | | syndiotactic | |
|---|---|---|---|---|---|
| | model | $J_{01}$ | $J_{02}$ | $J_{01}$ | $J_{02}$ |
| calculated according to Haasnoot et al. (eq 8 of ref 11, parameter set C) | I-A | 7.44 | 6.47 | 8.80 | 5.41 |
| | I-B | 7.76 | 6.06 | 8.82 | 5.28 |
| | II-A | 6.99 | 6.03 | 8.44 | 4.85 |
| | II-B | 7.24 | 5.69 | 8.46 | 4.74 |
| calculated with Karplus equation (parameter set III of ref 12) | II-A | 6.77 | 5.92 | 8.05 | 4.91 |
| | II-B | 6.98 | 5.60 | 8.05 | 4.79 |
| | ref 1 | 6.7 | 5.9 | 7.6 | 5.2 |
| observed | | 7.0 | 5.7 | 8.3 | 4.8 |

[a] Calculated values at 140 °C. Observed values[3] at 150 °C for the isotactic polymer and at 130 °C for the syndiotactic polymer.

chain, while in the case of the isotactic polymer the former model underestimates the difference $J_{01} - J_{02}$ and the latter one overestimates it. The different behavior originates mainly from the population of the dyad state tt* (in Suter and Flory's notation), which in model B is about twice as large as in A.

(iv) The Karplus equation derived from the analysis of 1,3,5,7-tetramethylcyclooctanes[12] yields results quite similar to the equation of Haasnoot et al.[11] Model II-B seems somewhat superior to II-A when this Karplus equation is used.

(v) Both models II-A and II-B reproduce the four values of $J_{0k}$ with equal or better accuracy than the method of Brückner et al.[1] In light of the present results, the conclusions reached by these authors concerning the relative populations of the less stable states seem questionable. For example, according to Brückner et al., in the isotactic chain the easiest helix inversion (in the sense which involves a syn–axial interaction) occurs via the conformational sequence /tg/g*t/gt/. In both models A and B the /g*t/ state is unfavored by an extra gauche interaction, as was indicated by the results of energy calculations[9,10] based on interactions between all atoms (i.e., including all the hydrogen atoms). This suggests that the stabilization of the /g*t/ state in the calculations of Brückner et al.[1] may be an artifact arising from considering the methyl groups and the terminal $CH_x$ groups of a dyad as spherical pseudoatoms. According to model B the inversion occurs mainly through states /tt*/, while according to A inversions via distorted /tg/gt/ states are about as probable as via /tt*/. At present it appears that different models can allow approximately the same flexibility to the chain, but the balance between different states is still subject to some degree of uncertainty.

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## Steric Energy of the Rotational State of the Side Groups of Poly(vinylnaphthalene)

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Poly(1-vinylnaphthalene) (PlVN) and poly(2-vinylnaphthalene) (P2VN) molecules have bulkier side groups than polystyrene (PS) derivatives. The steric conformation of these naphthyl side groups in polymers in solution and dynamic properties of poly(vinylnaphthalene) (PVN) in solution have attracted the interest of investigators in the fields of NMR spectroscopy[1] and fluorescence spectroscopy.[2-4]

Although P2VN and P1VN are isomeric, they exhibit rather different properties in solution; the behavior of the former resembles that of PS. Transitions are observed at about 50–80 °C in P2VN[5] and PS[6] in solution and the $^1H$ NMR spectral patterns are similar.[1] The differences between P1VN and P2VN are possibly due to differences in their rotational isomeric states (RIS). The phenyl group in PS has a $C_{2v}$ symmetry axis along the plane of the ring and there is no RIS for the side group. Presumably in P1VN, the 1-naphthyl group may be limited to a single conformation, which may be different from those for the 2-naphthyl or phenyl groups.

In order to elucidate the RIS of the pendant groups in P1VN and P2VN, we estimated the steric energy of the

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