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# Are the Steric Effects on the $^{13}$C-NMR Chemical Shifts of Hydrocarbon Polymers Really Long Range?

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ABSTRACT: It is demonstrated that the stereosequence-dependent $^{13}$C-NMR chemical shifts observed in hydrocarbon polymers can be satisfactorily understood on the basis of the $\gamma$ effect. Carbon atoms separated by three bonds and in a gauche arrangement, or conformation, are more shielded by ca. 5 ppm than when in the trans arrangement. The probability of finding the two carbon atoms in the gauche conformation, and therefore the probability of the $\gamma$ effect, depends on longer range stereoregularity, but it is the interaction between carbons separated by three bonds ($\gamma$), and not four ($\delta$), five ($\epsilon$), or six ($\xi$) bonds, which is responsible for the shielding.

It has recently been demonstrated on poly(propylene) model compounds[1,2] and ethylene–propylene copolymers[3] that their stereosequence-dependent $^{13}$C-NMR chemical shifts can be explained by the $\gamma$ effect. Based on $^{13}$C-NMR studies of paraffinic hydrocarbons,[4-7] it appears that the gauche arrangement of carbon atoms separated by three bonds ($\gamma$ substituents) results in an upfield shift ($\gamma$ effect) relative to the shielding experienced in the trans planar or anti conformation (see Figure 1).

The magnitude of the $\gamma$ effect experienced by a given carbon in a hydrocarbon polymer should depend on the proportion or probability of those bond conformations which produce a gauche arrangement between the carbon atom of interest and those carbon atoms attached in the $\gamma$ position. Bond rotational state probabilities are known[8,9] to be sensitive to the stereosequence of asymmetric polymer chains in the vicinity of the bond in question. Thus, the $^{13}$C-NMR chemical shift pattern observed for an asymmetric polymer is directly related to its conformational characteristics (bond rotation probabilities) as influenced by the chain's stereosequence.

$^{13}$C-NMR chemical shifts observed in the poly(propylene) model compounds 3,5-dimethylheptane,[10] 3,5,7-trimethylnonane,[10] and 3,5,7,9,11,13,15-heptamethylheptadecane[11] have been sucessfully calculated[1,2] through utilization of the $\gamma$ effect and the conformational characteristics of poly(propylene). In addition, the $^{13}$C chemical shifts observed[13-15] at each of the methylene carbons in the isolated ethylene fragments (–CH$_2$–CH$_2$–CH$_2$–) of ethylene–propylene (E–P) copolymers of low ethylene content can also be understood,[3] based on the $\gamma$ effect, as a function of the stereosequence of the surrounding poly(propylene) chain segments.

Recently Zetta et al.[16] have reported the $^{13}$C chemical shifts observed in poly(1-methyltetramethylene) (P1MTM), which can be considered as a regularly alternating E–P copolymer (see Figure 2). Using specialized resolution enhancement techniques, they were able to detect steric fine structure in the methyl ($C_{1'}$) and methylene ($C_{2,4}$)[17] resonances at high temperature (410 K) in 1,2,4-trichlorobenzene solutions.

Even though the asymmetric centers in P1MTM are separated by four bonds, as opposed to two in vinyl polymers, the stereoconfiguration of neighboring centers still apparently influences the local polymer chain conformation. Since neighboring methyl carbons are six bonds apart, or $\xi$ to each other, Zetta et al.[16] denoted this observed long-range steric sensitivity as the $\xi$ effect.

The use of the term $\xi$ effect, as well as the terms $\delta$ and $\epsilon$ effects, to describe the long-range stereosequence sensitivity of $^{13}$C-NMR chemical shifts is unfortunate. Clearly the chemical shift of a methyl carbon in P1MTM depends on the stereo disposition of neighboring methyl groups which are $\xi$ to the methyl carbon in question. However, this long-range dependence results from the influence of neighboring methyls on the bond rotation probabilities for the $C^{\alpha}_{1}$–$C^{\beta}_{2,4}$ bonds (see Figure 2) which determine the magnitude of the $\gamma$ effect of the $C_3$ carbons on the methyl

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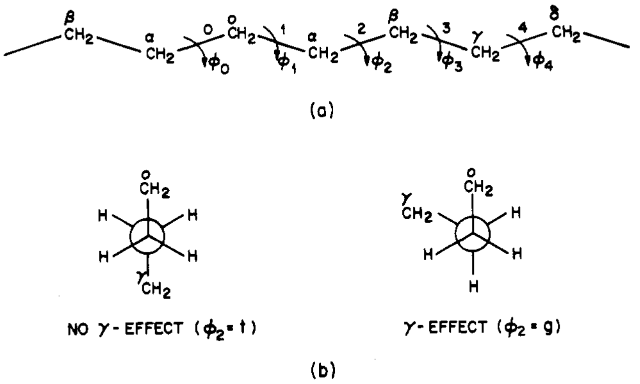

**Figure 1.** (a) Portion of a paraffinic hydrocarbon chain in the all-trans (*t*), planar zigzag conformation. (b) Newman projections along bond 2 in (a) illustrating the $\gamma$ effect.

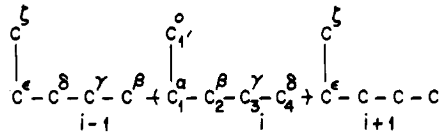

**Figure 2.** Portion of the P1MTM or regularly alternating E–P copolymer chain.

Table I
Calculated and Observed $^{13}$C-NMR Chemical Shifts for P1MTM

$$(-\overset{\overset{C_1'}{|}}{C_1}C_2C_3C_4-)_n$$

| carbon$^b$ | $\nu$,$^a$ ppm calcd$^c$ | $\nu$,$^a$ ppm obsd$^{16}$ |
|---|---|---|
| $C_1'(mm)$ | 0.0 | 0.0 |
| $C_1'(\begin{smallmatrix}rm\\mr\end{smallmatrix})$ | −0.02 | −0.03 |
| $C_1'(rr)$ | −0.04 | −0.06 |
| $C_1(mm)$ | 0.0 | 0.0 |
| $C_1(\begin{smallmatrix}rm\\mr\end{smallmatrix})$ | <−0.01 | 0.0 |
| $C_1(rr)$ | −0.01 | 0.0 |
| $C_{2,4}(m)$ | −0.03 | −0.04 |
| $C_{2,4}(r)$ | 0.0 | 0.0 |
| $C_3(m)$ | <−0.01 | 0.0 |
| $C_3(r)$ | 0.0 | 0.0 |

[a] Most downfield resonance of each carbon type assigned $\nu = 0.0$ ppm. [b] $m$, $r$ = meso, racemic dyad arrangement of methyls. [c] $\gamma = -5.3$ ppm; $T = 410$ K.

group. Neighboring methyl groups do not interact directly, but instead influence the conformations of the bonds in their vicinity.

Calculated $^{13}$C chemical shifts for the carbons in P1MTM are presented in Table I for comparison with the chemical shifts observed by Zetta et al.[16] A $\gamma$ effect of −5.3 ppm was adopted based on results obtained for poly(propylene) model compounds[1,2] and E–P copolymers.[3] Mark's[19] rotational isomeric state model of E–P copolymers was used to calculate bond rotation probabilities in the usual manner[20] as a function of P1MTM stereosequence.

It is clear that both the calculated and observed stereosequence dependencies of the $^{13}$C chemical shifts are small for P1MTM providing further confirmation for the conclusions reached in a previous study[3] of E–P copolymers of low ethylene content. Furthermore, there is good agreement between calculated and observed chemical shifts for all carbon atoms.

It is the direct interaction between carbon atoms $\gamma$ and not $\xi$[21] to each other which determines their chemical shifts, although $\xi$ substituents do indirectly influence the probabilities of the $\gamma$ interactions in a predictable manner. To term the influence of $\xi$ substituents on $^{13}$C-NMR chemical shifts the $\xi$ effect is to obscure their real direct source, namely the shorter range $\gamma$ effect.

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