Stereosequence-Dependent ^{13}C-NMR Chemical Shifts of Polystyrene Oligomers

Alan E. Tonelli

Bell Laboratories, Murray Hill, New Jersey 07974. *Received November 30, 1978*

ABSTRACT: Stereosequence-dependent ^{13}C-NMR chemical shifts are calculated for the polystyrene oligomers 2,4-diphenylpentane (2,4-DPP), 2,4,6-triphenylheptane (2,4,6-TPH), and 2,4,6,8-tetraphenylnonane (2,4,6,8-TPN). Calculated chemical shifts are obtained by quantitatively accounting for the number of γ interactions, or gauche arrangements, between carbon atoms separated by three bonds, i.e., carbons γ to each other. In addition, the effect of the magnetic shielding produced by phenyl groups that are first and second neighbors along the chain in either direction from a given carbon atom is considered. Agreement between calculated and observed (Jasse et al.) ^{13}C-NMR chemical shifts is good for each of the polystyrene model compounds. For all but the methine carbons, phenyl ring current contributions to the calculated chemical shifts are found to be small in comparison to the dominant γ effects. Comparison of the ^{13}C chemical shifts calculated for the central methylene carbons in 2,4-DPP, 2,4,6-TPH, and 2,4,6,8-TPN with those calculated for the 20 different stereoisomers of 2,4,6,8,10,12-hexaphenyltridecane (2,4,6,8,10,12-HPTD) indicate the extreme long-range nature of the stereosequence dependence of ^{13}C-NMR chemical shifts in polystyrene. Only in 2,4,6,8,10,12-HPTD do the conformational characteristics, and therefore the magnetic environment and resulting ^{13}C chemical shifts, closely approximate the environment of a methylene carbon in the various steroisomeric sequences of polystyrene.

^{13}C-NMR spectroscopy[1-3] has been demonstrated as the most powerful experimental probe of stereoconfiguration and/or sequence distribution in the asymmetric vinyl homo- and copolymers. Although the connections between stereosequences and ^{13}C-NMR spectra have been drawn[1,3] numerous times for many different vinyl polymers, determination of the stereoregularity of polystyrene via ^{13}C-NMR spectroscopy has proved elusive.[3-5]

As an example of the difficulty encountered in the interpretation of polystyrene ^{13}C-NMR spectra, it has been observed[6] that the methylene carbon portion of an atactic polystyrene spectrum consists of multiple resonances spread over ~5 ppm. Moreover the pattern of observed resonances is highly sensitive to the solvent employed in the ^{13}C-NMR experiment.

Recently Jasse et al.[7] have reported the synthesis,[8] separation, and ^{13}C-NMR spectra of the stereoisomers of 2,4-diphenylpentane (2,4-DPP), 2,4,6-triphenylheptane (2,4,6-TPH), and 2,4,6,8-tetraphenylnonane (2,4,6,8-TPN) as model compounds of polystyrene. From the aromatic C(1′) carbon (see Figure 1) chemical shifts observed in 2,4,6,8-TPN they proposed an assignment of the corresponding pentads of polystyrene. However, it is known[9-11] from ^{1}H-NMR spectra of polystyrene that the methine proton chemical shifts are dependent upon stereosequence to the level of nonads.

In an attempt to extend our studies[12-16] of the ^{13}C-NMR chemical shifts of vinyl polymers to those containing aromatic groups in their side chains, such as polystyrene, we have calculated the ^{13}C chemical shifts expected at the carbon atoms in the various stereoisomers of the polystyrene oligomers 2,4-DPP, 2,4,6-TPH, 2,4,6,8-TPN, 2,4,6,8,10,12-hexaphenyltridecane (2,4,6,8,10,12-HPTD), and 2,4,6,8,10,12,14,16-octaphenylheptadecane (2,4,6,8,10,12,14,16-OPHD). We hoped to understand the ^{13}C-NMR chemical shifts observed by Jasse et al.[7] and to learn at what degree of polymerization these oligomers become faithful model compounds of polystyrene.

^{13}C-NMR studies[17-20] of paraffinic hydrocarbons have made apparent the fact that the gauche arrangement (see Figure 2) of carbon atoms separated by three bonds (γ substituents) results in an upfield shift (γ effect) relative to the shielding experienced in the trans planar or anti conformation. The magnitude of the γ effect experienced by a given carbon atom in a vinyl polymer depends on the proportion or probability of those bond conformations which produce a gauche arrangement between the carbon atom of interest and any carbon atom attached in the γ position.

It is known[9,10,21,22] that the probability of finding any given vinyl polymer backbone bond in a particular rotational state depends on the stereosequence of the chain in the vicinity of that bond. Consequently the ^{13}C chemical shift pattern observed for a vinyl polymer is directly related to its conformational characteristics as determined by the stereoregularity of the chain.

Coupling of the γ effect with the conformational characteristics of vinyl polymer chains has led[12-16] to the correct prediction of ^{13}C-NMR chemical shifts for the carbon atoms in polypropylene and its model compounds,[12,14] ethylenepropylene copolymers,[13,16] and poly(vinyl chloride) and its model compounds.[15] This same procedure is applied in the present study to the oligomers of polystyrene in an attempt to explain their ^{13}C-NMR spectra and to eventually aid in the interpretation of the complicated spectra observed for polystyrene.

Description of the Calculations[23]

Bond rotational state probabilities were calculated in the usual manner[24] through adoption of the polystyrene conformational characteristics derived by Yoon et al.[25] Because steric interactions involving the bulky phenyl group preclude $\bar{g}$ conformations, the backbone bonds in polystyrene are limited to just two rotational states, the trans (t) and gauche (g) conformations.[26]

γ interactions resulting in upfield shifts of the methyl, methylene, and methine[28] carbons were assigned a magnitude of −5.3 ppm based on our previous studies[12-16] of vinyl polymers. For the C(1) aromatic carbon atoms the γ effect was halved based on ^{13}C-NMR studies[29] of alkylbenzenes.

In addition to the γ effect, the ring currents of the phenyl groups in polystyrene may also affect[9,10] the ^{13}C-NMR chemical shifts in a manner which depends on chain stereoregularity. Yoon and Flory[10] evaluated the ring current effects on the ^{1}H chemical shifts of the methine and aromatic protons in polystyrene and found them to be stereosequence dependent and relatively large. For this reason, we have accounted for the effects of phenyl group ring currents on the ^{13}C chemical shifts of the backbone

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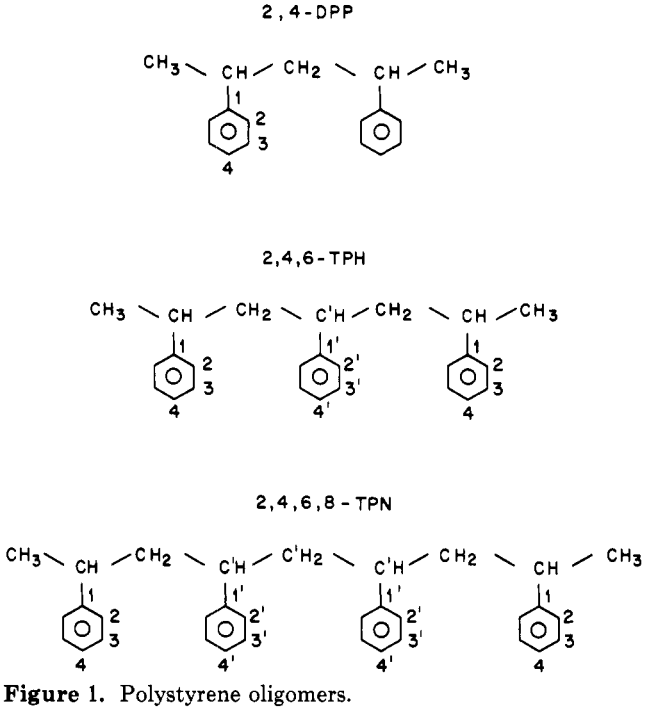

Figure 1. Polystyrene oligomers.

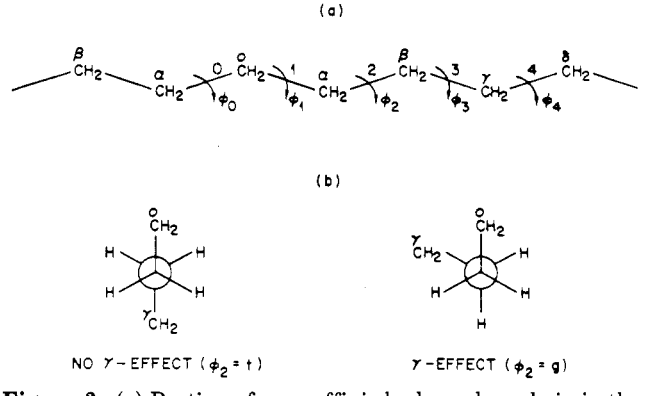

Figure 2. (a) Portion of a paraffinic hydrocarbon chain in the all-trans, planar zigzag conformation. (b) Newman projections along bond 2 in (a) illustrating the γ effect.

and C^1 aromatic carbon atoms in each of the polystyrene oligomers treated here.

The bond lengths and valence angles used by Yoon and Flory[10] were adopted. Each of the phenyl rings was restricted[25,31,32] to ±20° deviations (in 10° increments) from the orientation where its plane bisects the backbone valence angle at the methine carbon to which it is attached. Backbone bonds were permitted to adopt[25] either the trans (t) or gauche (g) states with rotation angles 0–20° or 100–120°, respectively, in 5° increments.

The coordinates of each backbone and the C(1) aromatic carbon atoms were calculated in the reference frames[33] of the first and second neighbor phenyl groups in either direction along the chain from each carbon for all possible backbone conformations. The Johnson–Bovey[34] table of chemical shift parameters, δ, expressed in ppm for a carbon located z phenyl ring radii above and perpendicular to the phenyl ring plane and ρ phenyl ring radii from the center of, but in the phenyl ring plane, were used to obtain the ring current chemical shifts. The chemical shift of each backbone conformation was then weighted by its probability to obtain the overall average shift expected for each stereoisomer.

No attempt was made to consider the effects of solvent on the calculated ^{13}C-NMR chemical shifts.

Table I
Computed Ring Current Chemical Shifts (δ) for the Carbon Atoms in 2,4-DPP

carbon atom	δ,[a] ppm	
	r[b]	m
CH_3	−0.12	0.0
CH	−0.05	0.0
C(1)	0.0	−0.10

[a] Negative values of δ indicate upfield chemical shifts. [b] m, r ≡ meso, racemic.

Table II
Computed Ring Current Chemical Shifts (δ) for the Carbon Atoms in 2,4,6-TPH

carbon atom	δ,[a] ppm		
	rr[b]	rm, mr	mm
CH_3	−0.19	−0.11, −0.09	0
CH_2	−0.12	0.0, −0.12	0.0
CH	−0.09	−0.14, 0.0	−0.08
CH′	−0.19	−0.09, −0.09	0.0
C(1)	−0.13	0.0, −0.16	−0.06
C(1′)	0.0	−0.08, −0.08	−0.17

[a] Negative values of δ indicate upfield chemical shifts. [b] m, r ≡ meso, racemic.

Table III
Comparison of Calculated and Observed ^{13}C-NMR Chemical Shifts (ν) in 2,4-DPP

carbon atom	ν,[a] ppm			
	m		r	
	obsd	calcd[b]	obsd	calcd[b]
C(1)	0.0	0.0	−0.4	−0.4
CH	−0.3	0.0	0.0	−0.1
CH_2	0.0	0.0	−0.3	0.0
CH_3	−1.2	−0.9	0.0	0.0

[a] Most downfield resonance of each carbon type is assigned ν = 0.0 ppm. [b] Includes γ effect and phenyl ring current shifts.

Table IV
Comparison of Calculated and Observed ^{13}C-NMR Chemical Shifts (ν) in 2,4,6-TPH

carbon atom	ν,[a] ppm					
	mm		mr (rm)		rr	
	obsd	calcd[b]	obsd	calcd[b]	obsd	calcd[b]
C(1)			−0.4	−0.3		
	0.0	0.0	−1.3	−1.3	−1.0	−1.2
C(1′)	−0.2	−0.6	−0.2	−0.3	0.0	0.0
CH			−0.1	0.0		
	−0.5	−0.1	−0.6	−0.1	0.0	−0.1
CH′	0.0	0.0	−0.2	−0.1	0.0	−0.2
CH_2			0.0	0.0		
	−0.6	−0.3	−1.4	−1.3	−0.8	−0.9
CH_3			0.0	0.0		
	−2.6	−2.5	−2.5	−2.2	−0.4	−0.4

[a] Most downfield resonance of each carbon type is assigned ν = 0.0 ppm. [b] Includes γ effect and phenyl ring current shifts.

Calculated Results and Discussion

Tables I and II present the effects of phenyl ring currents on the ^{13}C chemical shifts calculated for 2,4-DPP and 2,4,6-TPH. The maximum difference in expected ring current shifts for a given carbon between the stereoisomeric oligomers is <0.2 ppm. We shall soon see that ring current effects of this magnitude serve only as minor pertubations

Table V
Comparison of Calculated and Observed ^{13}C-NMR Chemical Shifts (ν) for 2,4,6,8-TPN

carbon atom	ν,[a] ppm											
	rrr		*rrm*		*rmr*		*mmr*		*mrm*		*mmm*	
	obsd	calcd[b]	obsd	calcd[b]	obsd	calcd[b]	obsd	calcd[b]	obsd	calcd[b]	obsd	calcd[b]
C(1)			−0.3	−0.4			−0.2	−0.1				
C(1′)	−1.1	−1.2	−1.0	−1.1	−1.4	−1.4	−1.3	−1.4	−0.5	−0.5	0.0	0.0
C(1′)			0.0	−0.2			−0.1	0.0				
	−0.5	−0.6		−0.7	−0.3	−0.2	−0.5	−0.2	−0.9	−0.5	−0.4	0.0
CH			0.0	0.0			0.0	0.0				
	0.0	−0.1	−0.6	−0.1	0.0	0.0	−0.6	−0.2	−0.6	−0.2	−0.7	−0.1
CH′			−0.2	−0.2			−0.3	−0.2				
	0.0	−0.2		−0.2	−0.2	−0.2		−0.2	−0.4	−0.2	−0.2	−0.0
CH_2			0.0	−0.2			−0.8	−1.6				
	−0.4	−0.5		−0.2	−1.1	−2.0	−1.3	−2.4		0.0	−0.9	−1.9
CH_2	−1.5	−1.1	−2.1	−2.1	0.0	0.0	−0.8	−0.6		−3.0		−1.1
CH_3			−0.7	−0.6			0.0	0.0				
	−0.6	−0.7	−2.7	−2.2	0.0	−0.1	−2.7	−2.8	−2.3	−2.2	−2.9	−2.9

[a] Most downfield resonance of each carbon type assigned ν = 0.0 ppm. [b] Includes γ effect and phenyl ring current shifts.

Table VI
Calculated ^{13}C-NMR Chemical Shifts of the Central Methylene Carbon in Polystrene Oligomers

oligomer	most upfield stereoisomer	most downfield stereoisomer	$\Delta\nu$,[a] ppm
2,4-DPP	*m, r*	*r, m*	0.0
2,4,6,8-TPN	*mrm*	*rmr*	−3.4
2,4,6,8,10,12-HPTD	*m(mrm)m*	*m(rmr)m*	−5.3
2,4,6,8,10,12,14,16-OPHD	*rr(mrm)mm*	*mm(rmr)mm*	−5.4

[a] $\Delta\nu \equiv \nu$(most upfield stereoisomer) − ν(most downfield stereoisomer).

on the much larger γ effects.

Calculated ^{13}C-NMR chemical shifts are compared in Tables III–V to those observed at room temperature by Jasse et al.[7] in 10% $CDCl_3$ and *o*-dichlorobenzene solutions. Agreement between the predicted and observed ^{13}C chemical shifts is generally good, with sensitivity to stereosequence greatest for the methyl carbons. For all carbons except the methine, whose γ effects are expected[28] to be independent of stereosequence, ring current effects contribute only marginally to the calculated chemical shifts (compare Tables I and II with Tables III and IV).

The rather minor influence of phenyl ring current effects on the ^{13}C-NMR chemical shifts of these oligomers, and presumably also polystyrene, is the result of two factors. First the magnitude of the stereosequence-dependent γ effect is large by comparison. Second, those backbone conformations which bring phenyl rings close enough to a given carbon atom to produce large ring current shifts (comparable to γ effects) are not very likely. As an example, in the *tt* conformation of *meso*-2,4-DPP each C(1) carbon is apposed to a phenyl ring and would be expected[34] to be shielded by ~0.8 ppm. However, the meso *tt* conformation is only expected to occur in 3–4% abundance thereby reducing the impact of this potentially large shielding.

To test the range of ^{13}C chemical shift sensitivity to stereosequence in polystyrene and its oligomers, the chemical shifts expected at the central methylene carbons in 2,4-DPP, 2,4,6,8-TPN, 2,4,6,8,10,12-HPTD, and 2,4,6,8,10,12,14,16-OPHD due to γ effects were calculated. The results are presented in Table VI, where the overall spreads in the predicted ^{13}C chemical shifts between the various isomers of each oligomer are presented.

Clearly the central portions of the 2,4,6,8,10,12-HPTD stereoisomers are characterized by the same average conformtions as are the stereoisomers of 2,4,6,8,10,12,14,16-OPHD (almost identical $\Delta\nu$) and polystyrene.[35] Thus the methylene portions of the ^{13}C-NMR spectra of polystyrene should be sensitive to stereosequence up to, but not beyond, the hexad level.

Jasse et al.[7] attempted to assign pentad structure in the C(1) region of polystyrene based on the C(1′) aromatic ^{13}C-NMR chemical shifts observed for the six 2,4,6,8-TPN isomers. As these authors noted, 2,4,6,8-TPN is not, although 2,4,6,8,10-pentaphenyllundecane would be, an oligomeric model for polystyrene C(1) pentad structure. Furtheremore, the calculated ^{13}C chemical shifts presented in Table VI raise serious doubts regarding the assumed similarity of the conformational characteristics in the vicinity of C(1′) in 2,4,6,8-TPN and around a C(1) carbon in polystyrene. The C(1) carbons in polystyrene are most probably sensitive to stereosequence up to the heptad level.

With the aid of calculated chemical shifts due to the γ effect, we are currently attempting complete assignments of the resonances in the methylene and C(1) aromatic portions of the ^{13}C-NMR spectra of atactic polystyrene.

References and Notes

(1) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972, Chapter 7.
(2) A. R. Katritzky, D. E. Katritzky, and D. E. Weiss, *Chem. Br.*, **12**, 45 (1976).
(3) J. C. Randall, "Polymer Sequence Determination", Academic Press, New York, 1977.
(4) Y. Inoue, A. Nishioka, and R. Chûjô, *Makromol. Chem.*, **156**, 207 (1972).
(5) K. Matsuzaki, T. Uryu, T. Seki, K. Osada, and T. Kawamura, *Makromol. Chem.*, **176**, 3051 (1975).
(6) R. E. Cais, personal communication of unpublished results.
(7) B. Jasse, F. Lauprêtre, and L. Monnerie, *Makromol. Chem.*, 178, 1987 (1977).
(8) B. Jasse, *Bull. Soc. Chim. Fr.*, to be published.[7]
(9) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 43 (1970).
(10) D. Y. Yoon and P. J. Flory, *Macromolecules*, **10**, 562 (1977).
(11) H. J. Harwood and L. Shepherd, unpublished results cited in ref 10.
(12) A. E. Tonelli, *Macromolecules*, **11**, 565 (1978).
(13) A. E. Tonelli, *Macromolecules*, **11**, 634 (1978).
(14) A. E. Tonelli, *Macromolecules*, **12**, 83 (1979).
(15) A. E. Tonelli, F. C. Schilling, W. H. Starnes, Jr., L. Shepherd, and I. M. Plitz, *Macromolecules*, **12**, 78 (1979).
(16) A. E. Tonelli, *Macromolecules*, in press.

(17) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 727 (1961).
(18) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1969).
(19) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
(20) F. A. Bovey, "Proceedings of the International Symposium on Macromolecules", Rio de Janeiro, July 26–31, 1974, E. B. Mano, Ed., Elsevier, Amsterdam, 1975, p 169.
(21) P. J. Flory and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **88**, 2873 (1966).
(22) P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 327 (1969).
(23) All calculations were performed at 25 °C, the temperature employed in the ^{13}C-NMR measurements reported by Jasse et al.[7]
(24) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969, Chapter III.
(25) D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 776 (1975).
(26) Rotation angle conventions are described in ref 27.
(27) P. J. Flory, P. R. Sundararajan, and L. C. De Bolt, *J. Am. Chem. Soc.*, **96**, 5015 (1974).
(28) Because the backbone bonds in polystyrene are restricted to the t and g states, with $\bar{g}$ excluded, methine carbons are always in a gauche arrangement with either C(1)(t) or CH_2(g) regardless of stereosequence, and should not exhibit stereosequence-sensitive γ effects.
(29) W. R. Woolfenden, Ph.D. Thesis, University of Utah, 1965, as described in ref 30.
(30) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, pp 97–101.
(31) Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, **3**, 294 (1970).
(32) A. E. Tonelli, *Macromolecules*, **6**, 682 (1973).
(33) The x and y axes are in the plane of the phenyl ring with origin at its center, and the z axis is perpendicular to the phenyl ring plane completing the right-handed coordinate system. $\rho = (x^2 + y^2)^{1/2}$ and $z = z$.
(34) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
(35) The range of chemical shifts observed[6] in the methylene portions of the ^{13}C-NMR spectra of atactic polystyrene is ~5 ppm which agrees favorably with the 5.3 ppm spread calculated for the methylene carbons in the stereoisomers of 2,4,6,8,10,12-(HPTD) and 2,4,6,8,10,12,14,16-OPHD.

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

Alan E. Tonelli

Bell Laboratories, Murray Hill, New Jersey 07974. *Received December 18, 1978*

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 γ 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 γ effect, depends on longer range stereoregularity, but it is the interaction between carbons separated by three bonds (γ), and not four (δ), five (ϵ), or six (ξ) 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 γ 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 (γ substituents) results in an upfield shift (γ effect) relative to the shielding experienced in the trans planar or anti conformation (see Figure 1).

The magnitude of the γ 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 γ 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 γ 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 γ 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 ξ to each other, Zetta et al.[16] denoted this observed long-range steric sensitivity as the ξ effect.

The use of the term ξ effect, as well as the terms δ and ϵ 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 ξ 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^{α}_1–$C^{\beta}_{2,4}$ bonds (see Figure 2) which determine the magnitude of the γ effect of the C_3 carbons on the methyl

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