tertiary nitrogen (high I and low C, F, and G). The moderate level of methylol on secondary nitrogen is consistent with the low F:U ratio (1.7) and absence of any cure treatment.

(ii) Samples II, III-1, and III-2 should be similar except that the degree of cure should be in the order III-2 ≫ III-1 > II. Thus, the methylols on secondary nitrogens (resonance E) should increase in that same order and the concentration of branching tertiary nitrogens (resonance G) should decrease.

A comparison of carbonyl line widths (resonance A) shows the peaks of the two ^{15}N-containing polymers to be sharper than those of the corresponding ^{14}N-containing resins. (A comparison of other line widths may be less meaningful, because of overlaps of resonances.) This is consistent with the ^{14}N effects discussed above.

Finally, the CP/MAS ^{13}C NMR technique provides a convenient, direct way to follow the chemistry of the curing process, as shown in Figure 8. In this example, intensity is decreasing from the region about 65 ppm, while it is concurrently increasing in the 55-ppm region as curing progresses. Thus, methylol end groups (resonance E)—and possible ether groups (resonance D)—decrease with cure while branching tertiary nitrogens (resonance G) increase.

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Registry No. Urea-formaldehyde copolymer, 9011-05-6.

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

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ABSTRACT: ^{13}C NMR chemical shifts are calculated for the various stereosequences present in atactic polystyrene. 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. The effects of magnetic shielding produced by the ring currents from phenyl groups that are first and second neighbors along the chain in either direction from a given carbon atom are also considered. ^{13}C NMR chemical shifts calculated to the hexad level of stereosequence are presented for the methylene carbons and to the heptad and pentad levels for the C(1) and C(4) carbons of the phenyl groups. The overall spreads (~4 ppm for CH_2, ~1 ppm for C(1), and ~0.5 ppm for C(4)) and ordering of the resonances observed in the ^{13}C NMR spectra of atactic polystyrene are generally reproduced by the calculated chemical shifts. This agreement aids the analysis of polystyrene stereosequence via ^{13}C NMR.

The connections between stereosequences and ^{13}C NMR spectra have been drawn[1-4] numerous times for many different vinyl polymers. However, for polystyrene, determination of its stereoregularity by ^{13}C NMR spectroscopy has proved elusive.[3,5-11] Long-range sensitivity to stereosequence (hexads for CH_2 and heptads for C(1) carbons) and some sensitivity to solvent of the observed ^{13}C NMR resonances in polystyrene have both contributed to the difficulty in their complete assignment.

Recently renewed experimental efforts have been made to assign the ^{13}C NMR spectra of atactic polystyrene. Jasse et al.[7] synthesized and separated the stereoisomers of several polystyrene oligomers, including 2,4,6,8-tetraphenylnonane (2,4,6,8-TPN). They recorded the ^{13}C NMR spectra of each and attempted a pentad assignment of polystyrene based on the ^{13}C chemical shifts observed for C(1) belonging to the internal phenyl groups. However, as noted by the authors, 2,4,6,8-TPN is not an oligomeric model compound for polystyrene C(1) pentad structure.

Harwood and co-workers[9] have measured the ^{13}C NMR spectra of partially epimerized isotactic polystyrenes. They interpreted the spectra by comparison with stereosequence distributions that were calculated by Monte Carlo simulation of the epimerization process. As an example, they concluded that the mm triad resonance of the methine carbon comes ~0.2 ppm downfield from the (mr and rm) and rr triads, with the latter separated by less than 0.05 ppm.

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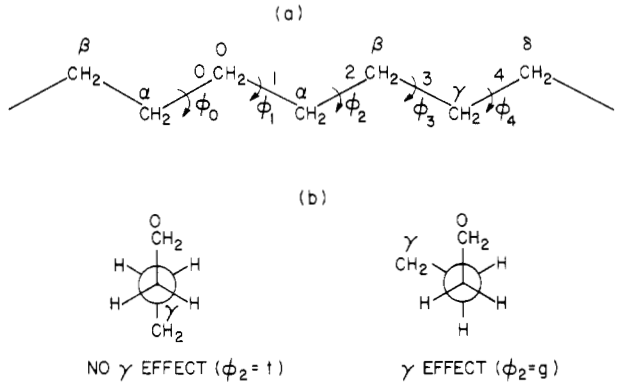

Figure 1. (a) Portion of a paraffinic hydrocarbon chain in the all-trans, planar zigzag conformation. (b) Newman projections along bond 2 in (a) illustrating the γ effect.

Most recently Sato et al.[11] synthesized 4,6,8,10,12-pentaphenylpentadecane (4,6,8,10,12-PPPD), an oligomeric model compound for polystyrene C(1) pentad stereosequences. Following separation of the stereoisomers of 4,6,8,10,12-PPPD, ^{13}C NMR spectra were recorded and resonances assigned. The oligomer assignments were used to assign the methylene carbon hexad and C(1) pentad resonances observed in the ^{13}C NMR spectrum of atactic polystyrene, even though 4,6,8,10,12-PPPD is not a true oligomeric model compound for polystyrene methylene carbon hexad stereosequences.

^{13}C NMR studies[12-15] of paraffinic hydrocarbons have made apparent that gauche arrangements (see Figure 1) of carbon atoms separated by three bonds (γ substituents) result in upfield shifts (γ effect) relative to the shielding experienced in the trans planar or anti conformation. The proportion or probability of those bond conformations that produce a gauche arrangement between the carbon atom of interest and any carbon atom attached in the γ position determines the magnitude of the γ effect experienced by that carbon atom in a vinyl polymer.

The probability of finding any given vinyl polymer backbone bond in a particular rotational state depends[16-19] on the chain stereosequence in the vinicity 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 local stereosequence of the chain.

Coupling of the γ effect with the conformational characteristics of vinyl polymer chains has led to the correct prediction[20] of ^{13}C NMR chemical shifts for the carbon atoms in polypropylene[21] and several of its oligomers,[22,23] ethylene–propylene copolymers,[24,25] poly(vinyl chloride) and its oligomers,[26] ethylene–vinyl chloride copolymers,[27] propylene–vinyl chloride copolymers,[28] and several fluoro polymers.[29]

The γ effect method of calculating ^{13}C NMR chemical shifts was also applied[30] successfully to the polystyrene oligomers studied by Jasse et al.[7] In addition to γ effects, the effects of the magnetic shielding produced by ring currents[31] in the phenyl groups that are first or second neighbors along the chain in either direction from a given carbon atom were also considered.[18,19]

In the present study we extend these calculations of ^{13}C NMR chemical shifts to the various stereosequences in polystyrene with the hope of assisting the task of assigning the resonances observed in the atactic polymer.

Description of Calculations

^{13}C NMR chemical shifts calculated as a function of polystyrene stereosequence were obtained as described[30] in our previous study of polystyrene oligomers. The

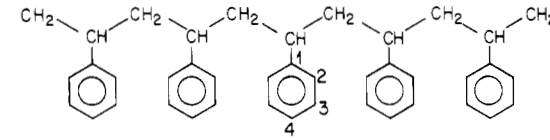

Figure 2. A schematic illustration of a pentad sequence in polystyrene.

Table I
^{13}C NMR Chemical Shifts Calculated at 100 °C for the Methylene Carbons in Polystyrene Hexad Stereosequences

no.	hexad stereosequence	δ[a]
1	mrmrm	0.0
2	rrmrm	−0.22
3	rrmrr	−0.42
4	mrrrm	−0.61
5	rrrrm	−0.85
6	mrmmr	−1.08
7	rrrr	−1.11
8	mrmmm	−1.27
9	rrmmr	−1.36
10	rrmmm	−1.44
11	mmmmr	−2.03
12	rmmmr	−2.04
13	mmmmm	−2.10
14	rmrrm	−2.25
15	mmrrm	−2.35
16	rmrrr	−2.51
17	mmrrr	−2.63
18	rmrmr	−4.00
19	rmrmm	−4.12
20	mmrmm	−4.24

[a] Includes γ effects and phenyl ring current contributions. Most downfield resonance assigned δ = 0.0 ppm.

shielding effect produced at a methylene carbon by a methine carbon in a gauche arrangement is −5.3 ppm, while each C(1) aromatic carbon is shielded by only half[30] this amount when in a gauche arrangement with a methine carbon (see Figure 2).

We have accounted for the effects of phenyl group ring currents on the ^{13}C chemical shifts of the backbone methylene and C(1) and C(4) aromatic carbons in each polystyrene stereosequence considered. Ring currents produced by the first and second neighbor phenyl groups in either direction along the chain from each carbon were considered.

Polystyrene stereosequences to the pentad, hexad, and heptad level were considered when ^{13}C chemical shifts were calculated for the C(4), methylene, and C(1) carbons, respectively.

Results and Discussion

^{13}C NMR chemical shifts calculated at 100 °C for the methylene carbons in each polystyrene hexad stereosequence are presented in Table I. Tables II and III contain the ^{13}C chemical shifts calculated for the aromatic ring carbons C(1) and C(4) at the heptad and pentad stereosequence level, respectively, also at 100 °C.

In Figures 3 and 4 the ^{13}C chemical shifts calculated for the methylene and C(1) aromatic carbons are compared to the observed resonances of atactic polystyrene as measured and assigned by Sato et al.[11] The width of the calculated pentad ^{13}C chemical shifts for C(1) reflect the sensitivity to heptad stereosequences as presented in Table II. ^{13}C NMR assignments for atactic polystyrene were taken from the work of Sato et al.,[11] because of the superior resolution of their spectrum, especially the methylene carbon region, and because their assignments are partially based on the observed resonances for the stereoisomers of the polystyrene model compound 4,6,8,10,12-PPPD. In

Table II
^{13}C NMR Chemical Shifts Calculated at 100 °C for the C(1) Aromatic Carbons in Polystyrene Heptad Stereosequences

heptad stereosequence	δ^a	heptad stereosequence	δ^a
m(mmmm)m	0.0	r(rmrm)r	−0.510
m(mmmm)r	−0.005	r(rmrm)m	−0.530
r(mmmm)r	−0.011	m(rmrm)r	−0.535
m(mmrm)r	−0.159	m(rmrm)m	−0.550
m(mmrm)m	−0.173	r(rrmr)r	−0.555
r(mmrm)r	−0.191	m(rrmr)r	−0.561
r(mmrm)m	−0.207	r(rrmr)m	−0.575
m(mmmr)r	−0.208	m(rrmr)m	−0.577
m(mmmr)m	−0.217	m(rrrr)m	−1.064
r(mmmr)r	−0.223	r(rrrr)m	−1.065
m(mmrr)r	−0.228	r(rrrr)r	−1.071
r(mmmr)m	−0.230	r(mrrr)m	−1.084
m(mmrr)m	−0.234	r(mrrr)r	−1.092
r(mmrr)r	−0.256	m(mrrr)m	−1.109
r(mmrr)m	−0.262	m(mrrr)r	−1.118
r(rmmr)r	−0.452	r(mrrm)r	−1.138
m(rmmr)r	−0.467	r(mrrm)m	−1.165
m(rmmr)m	−0.476	m(mrrm)m	−1.195

[a] Includes γ effects and phenyl ring current contributions. Most downfield resonance assigned δ = 0.0 ppm.

Table III
^{13}C NMR Chemical Shifts Calculated at 100 °C for the C(4) Aromatic Carbons in Polystyrene Pentad Stereosequences

pentad stereosequence	δ^a	pentad stereosequence	δ^a
mrrm	0.0	mmrr	−0.41
mrmm	−0.19	mmmm	−0.44
mrrr	−0.19	rrmr	−0.48
mrmr	−0.26	mmmr	−0.52
rrrr	−0.39	rmmr	−0.59

[a] Obtained from considering phenyl ring currents only. Most downfield resonance assigned δ = 0.0 ppm.

addition, these assignments are consistent with a Bernoullian polymerization mechanism with $P_r = 0.54$, a value we[32] also find for atactic polystyrene based on independent nonspectroscopic techniques.

Considering that Sato et al.[11] used the assignments of the central methylene carbons in 4,6,8,10,12-PPPD, which is not an entirely appropriate model for the hexad stereosequences in polystyrene, to arrive at these methylene hexad ^{13}C NMR assignments, the agreement between calculated and observed methylene ^{13}C chemical shifts is reasonable. The overall dispersion observed in the ^{13}C chemical shifts (~4.2 ppm) due to the various hexad stereosequences is closely reproduced by the calculated chemical shifts. From low to high field the predicted order of resonances (xrmry > xrrry > xrmmy > xmmmy ~ xmrry > xmrmy) is very similar to that observed in the methylene carbon portion of the ^{13}C NMR spectrum recorded and assigned for atactic polystyrene by Sato et al.[11] The inability to experimentally resolve and assign all the hexads containing the rmm, mmm, and mrr tetrads is the major reason for the differences in appearances in the line spectra presented in Figure 3.

The dispersion in ^{13}C NMR chemical shifts (~1 ppm) calculated for the C(1) aromatic carbons in the various heptad stereosequences of atactic polystyrene is very similar to the overall spread observed by Sato et al.[11] (see Figure 4). Also the calculated and assigned order of resonances from low to high field (xmmy > xmry > xrry) generally agree, though the C(1) chemical shifts calculated to the heptad level indicate mixing and overlap of some

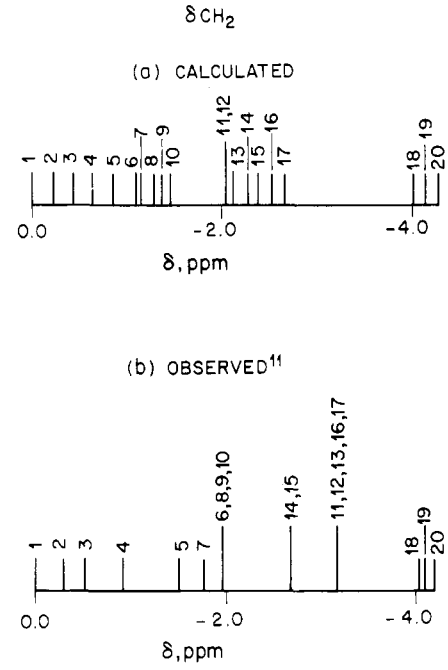

Figure 3. (a) Calculated and (b) observed[11] ^{13}C NMR chemical shifts for the methylene carbons in atactic polystyrene. See Table I for the correspondence between the line numbers and hexad stereosequences.

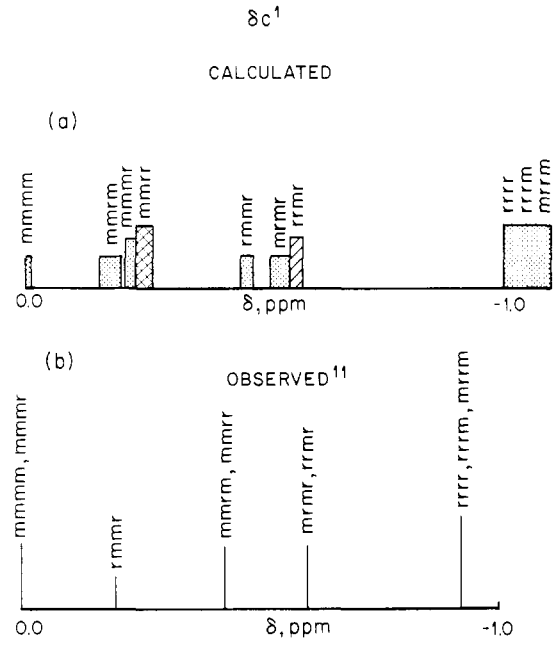

Figure 4. (a) Calculated and (b) observed[11] ^{13}C NMR chemical shifts for the C(1) aromatic carbons in atactic polystyrene. The widths of the calculated chemical shifts presented at the pentad level correspond to the sensitivity to longer heptad stereosequences (see Table II).

xmmy and xmry resonances. The tentative nature of the assignments of Sato et al.[11] and the observed[33] solvent sensitivity of the resonances in the C(1) aromatic carbon region of the spectra result in the minor differences seen in Figure 4.

C(4) aromatic carbon ^{13}C chemical shifts are uninfluenced by γ effects, because only C(1) is γ to C(4) and both are part of the rigid phenyl ring. The overall spread in ^{13}C chemical shifts calculated for C(4) through evaluation of ring current effects contributed by first and second neighbor phenyl groups in all pentad stereosequences is ~0.5 ppm (see Table III), in agreement with the observed[33]

spectra for atactic polystyrene.

Although the structureless nature of the C(4) portion of the ^{13}C NMR spectrum, a description that also characterizes the rather uniformly spaced calculated chemical shifts presented in Table III, prevents any stereosequence analysis, the agreement between the observed and overall spreads in C(4) chemical shifts indicates the adequacy of our method of evaluating ring current effects on the ^{13}C chemical shifts in polystyrene. Unlike C(4) carbons, the backbone methylene and C(1) aromatic carbons exhibit ^{13}C chemical shifts that are only marginally influenced by ring current effects as a consequence of the large γ effects experienced by each, which are several times greater than ring current contributions.

It is clear from Table III that first neighbor phenyl groups that are meso (m) to the observed C(4) contribute greater ring current shieldings than their racemic (r) counterparts. On the other hand, the racemic arrangement of phenyl groups in the terminal dyads of the pentad stereosequences contributes greater ring current shielding than their meso arrangement.

It can be concluded from the overall agreement between calculated and observed ^{13}C NMR chemical shifts that the stereosequence-dependent ^{13}C NMR chemical shifts observed in the spectra of atactic polystyrene have their principal origins in conformationally sensitive γ effects. Ring currents from neighboring phenyl groups make only a modest contribution to the magnetic shielding at the methylene and C(1) aromatic carbon nuclei, while for the methine and C(2), C(3), and C(4) aromatic carbons ring currents are the sole source of the much smaller observed chemical shift dispersion among the various stereosequences. Both of these conclusions were previously[30] reached for polystyrene oligomers whose observed[7] ^{13}C chemical shifts were also rationalized on the basis of γ effect and phenyl ring current shieldings.

With a few minor exceptions, which are as likely attributable to uncertainties in resonance assignments and/or solvent effects as due to failings in the calculated ^{13}C chemical shifts, the observed and assigned ^{13}C NMR spectrum of atactic polystyrene presented by Sato et al.[11] is in agreement with the ^{13}C chemical shifts calculated here. This strengthens the majority of their assignments and adds further support to their inference that atactic polystyrene is a Bernoullian polymer with $P_r = 0.54$.

After all the attempts[1-11] by numerous investigators to determine the stereosequence of atactic polystyrene by ^{13}C NMR, it appears that the major portion of this task has been successfully completed by Sato et al.[11] and corroborated by our calculated ^{13}C chemical shifts. We hope that the calculated ^{13}C chemical shifts we have presented will materially aid in the completion of this task.

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Registry No. Polystyrene, 9003-53-6.

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