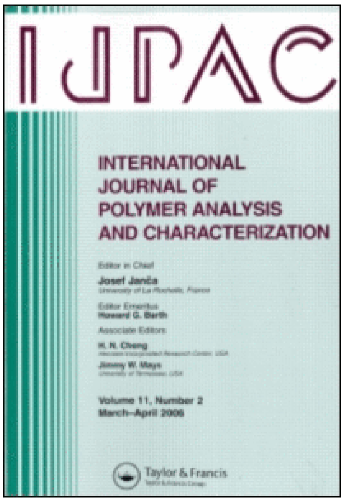

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NMR Studies of Polystyrene Tacticity

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NMR Studies of Polystyrene Tacticity

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The NMR spectral assignments of polystyrene are reviewed and re-examined using various NMR techniques. Revised ^{13}C-NMR assignments are obtained of the backbone methylene carbon; furthermore, the tacticity sequences of backbone methine carbon are assigned for the first time. The observed spectral intensities are fitted to a reaction probability model using curve deconvolution and a computer-assisted analytical approach. In addition, through the two-dimensional ^{1}H-^{13}C shift-correlated experiment, ^{1}H-NMR assignments are obtained. A spectral simulation approach, using a statistical model and observed ^{13}C shifts, is devised.

KEY WORDS Nuclear magnetic resonance (NMR), polystyrene, simulation approach, reaction probability model, tacticity, two-dimensional NMR.

INTRODUCTION

The tacticity of polystyrene is an old problem that has been repeatedly studied. Polystyrene was in fact among the first polymers examined by ^{1}H NMR [1]. The ^{1}H spectrum of the atactic polymer consists of several broad, overlapped resonances which do not easily provide information on tacticity. Nevertheless, over the years many attempts have been made to assign the ^{1}H spectrum of polystyrene [2–13]. The assignments have been assisted with deuteration [6,8,10], theoretical calculations [7], and epimerization [9,12]. A good understanding of the tacticity patterns has been achieved for the backbone methine proton [9,13] and aromatic ortho (C_2) protons [12].

Similarly, ^{13}C NMR has been used extensively for polystyrene, starting with the work of Johnson et al. [14]. Early on, several different assignment schemes were proposed [15–17]. These assignments were checked using statistical models for different samples of polystyrene [18–19]. Further efforts in ^{13}C assignments have been carried out via three approaches. First, low-molecular-weight model compounds have been made and the

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^{13}C assignments extrapolated to polymers by Sato et al. [20–23]. Secondly, epimerization reactions have been used elegantly in a series of papers by Harwood et al. [24–26]. Finally, the ^{13}C relative shifts have been calculated through γ-gauche rotational isomeric state model by Tonelli [27–28]. More recently, tacticity and assignments have been re-visited by Bahulekar et al. [29], Tsai et al. [30], and Kawamura et al. [31].

Through the work of these research groups, a consensus has emerged [23,26,28,31] on the ^{13}C NMR assignments of the aromatic C_1 carbon at the triad level and even for most of the pentads. However, there is a greater divergence of opinion on the assignments of the backbone methylene carbon. As for the other carbons (backbone methine and aromatic C_2, C_3, and C_4), complete ^{13}C assignments have not been made previously.

Experimental

Several polystyrene samples with different tacticities were included in this study. The samples were dissolved in 1,2,4-trichlorobenzene at 7–8 wt % concentrations with d_6-benzene added as the field/frequency lock material. Figures 1 and 4 were acquired on a Bruker AS-500 spectrometer, operating at 110°C. The rest of the NMR data were obtained on a GE Nicolet NT-300 spectrometer (^{13}C frequency = 75.46 MHz). The probe temperature was set at 110°–120°C.

The two-dimensional (2D) ^{13}C-^{1}H shift-correlated spectra were acquired using the CSCM pulse sequence included in the NMC-1280 software package. For ^{13}C, a sweep width of 6 kHz and 4K data points were employed. A total of 128 spectra were used to provide the equivalent of 1.5 kHz sweep width in the proton frequency dimension. Free induction decays in the proton frequency dimension were zero-filled before Fourier transformation and the spectra displayed in the absolute value mode. All chemical shifts were corrected to tetramethylsilane (TMS) at 0 ppm.

RESULTS AND DISCUSSION

Assignment of Aromatic C_1 (ipso) Carbon

The ^{13}C NMR spectrum of the aromatic C_1 carbon (144–146 ppm) is shown in Figure 1. In the literature, this spectrum is often split into three to six regions for the purpose of assignment and intensity determination. For illustration, six regions are indicated in Figure 1 and labelled A through F. Harwood et al. [26] and Tonelli [28] provided heptad assignments, whereas Sato et al. [23] and Kawamura et al. [31] made pentad assignments. The four assignment schemes are given in Table I.

At the triad level, all four assignment schemes tend to agree (mm > mr > rr, from low to high field). At the pentad level (using the six regions A-F), Harwood and Sato agree perfectly [23,26]. Tonelli's pentad assignments are similar except for the relative orderings in ^{13}C shifts for (mmrm), (mmmr), (mmrr), and (rmmr); this discrepancy may be due to solvent effects, as indicated by Tonelli [28]. The recent pentad assignments by Kawamura et al. [31] are compatible with Sato's and Harwood's schemes, except that (mmrr) and (mrmr) pentads are reversed. Kawamura et al. based their reverse assignment on a better fit with the observed intensities. This is curious because in the Bernoullian model both (mmrr) and

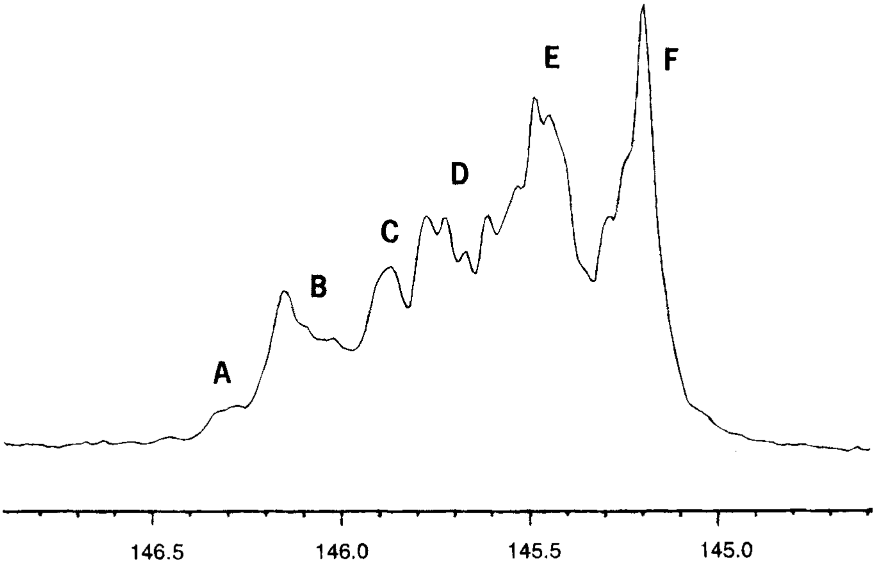


FIGURE 1 ^{13}C NMR spectrum of aromatic C_l carbon of atactic polystyrene (sample *a*) in 1,2,4-trichlorobenzene at ca. 115°C.

(mrmr) pentad have the same intensities; thus the proposed reverse assignment would not improve the fit. In addition, the shift position for (mmrr) in the reverse assignment would clearly contradict the shift position reported for the (mmmrrm) heptad by Longo et al. [32].

On the basis of triad assignments, the spectrum shown in Figure 1 (for atactic polystyrene, sample *a*) is consistent with a Bernoullian probability model with $P_m \approx 0.48$.

Assignment of Methylene Carbon

The backbone methylene ^{13}C resonates at 42–47 ppm, covering a large shift range. Because of the large spread in ^{13}C shift, one may expect more facile spectral assignments. This has not turned out to be the case. Although several assignment schemes have been published previously for the methylene carbon, there is as yet no consensus. For convenience, the more recent ^{13}C NMR assignment schemes [23,24,28,31] are summarized in Table II.

To assist in the assignments, we obtained the ^{13}C NMR spectra of polystyrene with different tacticities. For illustration, the spectra of three samples (isotactic, syndiotactic, and atactic) are given in Figure 2. As expected, the methylene carbons are split by tacticity into multiple peaks. There are at least 20 distinct spectral peaks as labelled on the spectra. Note that peaks 7 and 8, peaks 9 and 10, and peaks 15–17 are partially overlapped.

Our assignments are obtained systematically in five steps.

Step 1. Use the observed ^{13}C shifts of the isotactic, syndiotactic, and atactic polystyrene samples as the starting points.

Step 2. Observe the shifts of minor resonances in the spectra of isotactic and syndiotactic samples given in this work or reported in the literature [30,33].

TABLE I

Comparison of ^{13}C NMR assignments of C_1 carbon in polystyrene for chlorinated benzene solvent at 150°C

Region	No.	Shift	Harwood[a]	Tonelli[b]	Sato[c]	Kawamura[d]
A	1	146.40	m(mmmm)m	m(mmmm)m		m(mmmm)m
	2	146.32	m(mmmm)r	m(mmmm)r		
	3	146.25	r(mmmm)r	r(mmmm)r		m(mmmm)r
B	4	146.20	m(mmmr)r	m(mmrm)r	mmmm	r(mmmm)r
	5	146.18	r(mmmr)r	m(mmrm)m	mmmr	mmmr
	6	146.13	m(mmmr)m	r(mmrm)r		
	7	146.06	r(mmmr)m	r(mmrm)m		
C	8	146.01	r(rmmr)r	m(mmmr)r		
	9	145.92	m(rmmr)r	m (mmmr)m	rmmr	rmmr
	10	145.91	m(rmmr)m	r(mmmr)r		
D	11	145.85	m(mmrr)r	m(mmrr)r		
	12	145.77	m(mmrr)m	r(mmmr)m		
	13	145.76	r(mmrr)r	m(mmrr)m		
	14	145.70	r(mmrr)m	r(mmrr)r	mmrm	mmrm
	15	145.74	m(mmrm)r	r(mmrr)m	mmrr	mrmr
	16	145.67	m(mmrm)m	r(rmmr)r		
	17	145.63	r(mmrm)r	m(rmmr)r		
	18	145.60	r(mmrm)m	m(rmmr)m		
E	19	145.53	r(mrmr)r	r(rmrm)r		
	20	145.50	r(mrmr)m	r(rmrm)m		
	21	145.48	r(rmrr)r	m(rmrm)r		
	22	145.45	r(rmrr)m	m(rmrm)m	mrmr	mmrr
	23	145.43	m(rmrr)r	r(rrmr)r	rrmr	rrmr
	24	145.41	m(mrmr)r	m(rrmr)r		
	25	145.36	m(mrmr)m	r(rrmr)m		
	26	145.35	m(rmrr)m	m(rrmr)m		
F	27	145.27	m(rrrr)m	m(rrrr)m		
	28	145.20	r(rrrr)r	r(rrrr)m		
	29	145.15	m(rrrr)r	r(rrrr)r		
	30	145.12	r(mrrr)r	r(mrrr)m	rrrr	rrrr
	31	145.11	r(mrrr)m	r(mrrr)r	rrrm	rrrm
	32	145.07	m(mrrr)m	m(mrrr)m	mrrm	mrrm
	33	145.08	r(mrrm)r	m(mrrr)r		
	34	145.06	m(mrrr)r	r(mrrm)r		
	35	145.00	m(mrrm)r	r(mrrm)m		
	36	144.94	m(mrrm)m	m(mrrm)m		

[a] Taken from ref. [26].

[b] Taken from ref. [28], based on the relative shifts reported.

[c] Taken from ref. [23].

[d] Taken from ref. [31].

Step 3. Make judicious use of previously published assignments [20–33].

Step 4. Compare the intensities of the resonances to resolve difficult assignments. The use of necessary relationships and reaction probability models has been helpful in this connection.

Step 5. Match with 2D ^1H-^{13}C shift correlated data to check for obvious errors.

The assignments derived at each step are summarized in Table III. Steps 1 and 2 permitted unambiguous assignments for eight hexads and tentative assignments for two hexads. In Step 3, eight peaks were assigned on the basis of earlier work [23,24,28,31].

TABLE II

Comparison of different ^{13}C NMR assignment schemes for the methylene carbon of polystyrene[a]

	Harwood[b]		Tonelli[c]		Sato[d]		Kawamura[e]	
No.	shift	scheme	shift	scheme	shift	scheme	shift	scheme
1	46.58	rrmrr	0	mrmrm	46.73	mrmrm	46.7	mrmrm
2	46.32	rrmrm	–0.22	rrmrm	46.44	rrmrm	46.4	rrmrm
3	46.06	mrmrm	–0.42	rrmrr	46.22	rrmrr	46.2	rrmrr
4	45.72	rrrrr	–0.61	mrrrm	45.61	mrrrm	45.8	mrrrm
5	45.20	mrrrr	–0.85	mrrrr	45.22	mrrrr	45.2	mrrrr
6	44.90	rrmmr	–1.08	mrmmr	44.95	rrrrr	44.9	
7	44.68	rrmmm	–1.11	rrrrr			44.7	mrmmr, r(mrmmm)x
8	44.68	mrrrm	–1.27	mrmmm	44.79	mmr		
9	44.64	mrmmr	–1.36	rrmmr			44.6	rrmmm, m(mrmmm)x
10	44.42	mrmmm	–1.44	rrmmm				rmmrr, rrrrr
11	44.16	rmmmr	–2.03	mmmmr	44.05	rmrrm	44.2	mmrrr
12	43.95	mmmmr	–2.04	rmmmr		mmrrm	44.0	rmrrr
13	43.90	mmrrr	–2.10	mmmmm				
14	43.73	mmmmm	–2.25	rmrrm		rmrrr		mmrrm
15	43.47	rmrrr	–2.35	mmrrm	43.59	mmrrr	43.5	rmrrm
16	43.38	mmrrm	–2.51	rmrrr		mmm		mmm
17	43.12	rmrrm	–2.63	mmrrr				
18	42.69	mmrmm	–4.00	rmrmr	42.70	rmrmr		rmrmr
19	42.43	rmrmm	–4.12	mmrmr	42.66	rmrmm	42.6	rmrmm
20	42.17	rmrmr	–4.24	mmrmm	42.55	mmrmm		mmrmm

[a] ^{13}C shifts for chlorinated benzene solvents at >100°C.

[b] Taken from ref.[24] data obtained at 120°C.

[c] Taken from ref.[28], only relative shifts reported.

[d] Taken from ref.[23], data obtained at 150°C.

[e] Taken from ref. [31] data obtained at 150°C, observed values corrected by –0.4 ppm for ease of comparison.

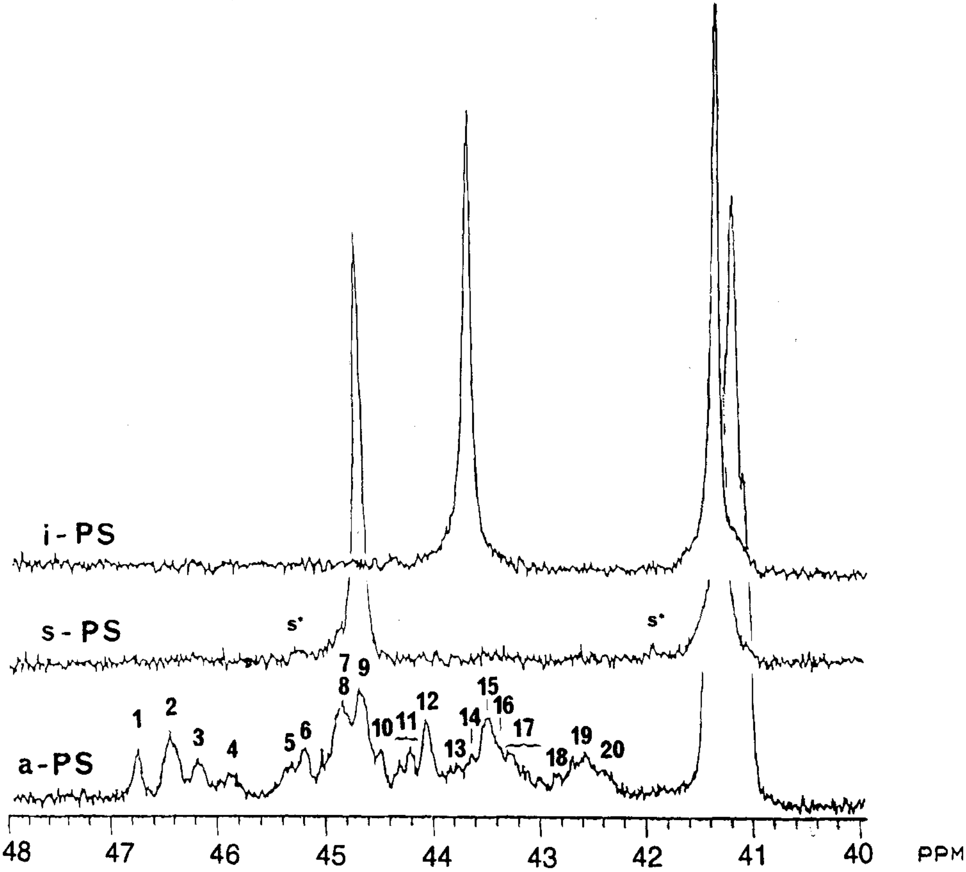


FIGURE 2 ^{13}C NMR spectra of the aliphatic carbons of atactic polystyrene (lower trace), syndiotactic polystyrene (middle trace), and isotactic polystyrene (upper trace), in 1,2,4-trichlorobenzene at ca. 115°C. The notation s* in the middle trace represents spinning side band.

Peak numbers 1, 2, 4, 18, 19, and 20 have been previously assigned by Tonelli, Sato, and Kawamura. The locations of (mrmmr) and r(mrmmm)x have been assigned differently by different workers; we prefer the latest assignments of Kawamura's [31].

Step 4 was achieved by taking into consideration the observed intensities of several polystyrene samples. An example is the atactic polystyrene (Sample *a*). Owing to spectral overlap, the observed intensities were obtained through curve deconvolution. The observed and resolved resonances are shown in Figure 3. The procedure was repeated, and the intensities corresponding to the components were found to be rather close. The average values were used as the observed intensities.

To fit the observed intensities to a reaction probability model (and to confirm assignments), we use the computer-assisted analytical (model-fitting) approach [34].

NMR data → Spectral assignments → Spectral intensities → Model fitting → Reaction probabilities

TABLE III

Assignment scheme for methylene ^{13}C in 1,2,4-trichlorobenzene at about 115°C, according to this work

No	^{1}H Shift	^{13}C Shift[a]	Steps 1–2	Step 3[b]	Steps 4–5[b]
1	1.53	46.79		mrmrm	mrmrm
2	1.46, 1.52	46.45		rrmrm	rrmrm
3	1.44	46.21	rrmrr	rrmrr	rrmrr
4	1.61	45.90, 45.84		mrrrm	mrrrm
5	1.56	45.37			m(mrrrr)x
6	1.53	45.22	mrrrr	mrrrr	r(mrrrr)x
7	1.56	44.89		mrmmr	mrmmr
8	1.56?	44.84		r(mrmmm)x	r(mrmmm)x
	1.56?	44.78			m(mrmmm)x
9	~ 1.51	44.68	rrrrr	rrrrr	rrrrr
		44.60	rrmmm (?)	rrmmm	rrmmm
					m(rmmrr)x
10	1.52	44.47	rmmrr (?)	rmmrr	r(rmmrr)x
11	1.60	44.32, 44.24			rmmmr
12	1.59?	44.07			rmrrm
13	1.59?	43.85, 43.76	mmmmr	mmmmr	mmmmr
14	1.59	43.66			r(mmmmm)x
		43.62	mmmmm	mmmmm	m(mmmmm)m
15	1.53	43.52	rmrrr	rmrrr	rmrrr
16	1.53	43.44	mmrrm	mmrrm	mmrrm
17	1.51	43.32	mmrrr	mmrrr	r(mmrrr)x
		43.18			m(mmrrr)x
18	1.59	42.88, 42.82		rmrmr	rmrmr
19	1.60	42.73, 42.61		rmrmm	rmrmm
20	1.60	42.52, 42.40		mmrmm	mmrmm

[a] The 30 ^{13}C shift values given in this column are used in the simulated spectrum shown in Figure 8.

[b] The symbol *x* denotes both *m* and *r*.

The polymer is assumed to obey first-order Markovian statistics. The theoretical expressions for the first-order Markovian reaction probabilities corresponding to all the n-ad sequences are shown in Table IV. As reported previously [34], the observed and the theoretical intensities are compared in this procedure through a simplex algorithm, and the optimal reaction probabilities are obtained.

Using our revised assignments (shown in the last column of Table III and in Table IV), we obtained good agreement between the observed and the calculated values for sample a. The mean deviation is 0.8. In conformity with the aromatic C_1 carbon data, the atactic polymer obeys Bernoullian statistics with $P_m = 0.48$.

For additional confirmation, we have also carried out the computations on the data reported by Kawamura et al. [31] Their data (Table V) had been acquired at a higher temperature (150°C). Under their experimental conditions, it appears that the (mrmmm)-centered octads move relatively further apart such that the r(mrmmm)x octads stay as peak 8, but the m(mrmmm)x octads are found under peak 9. (This presumption would also be consistent with Kawamura's assignments of the mrmmm- centered octads) [31]. Thus, in fitting Kawamura's data, we use our revised assignments, except for the location of the m(mrmmm)x octads. The agreement between the observed and the calculated intensities (Table V) is satisfactory.

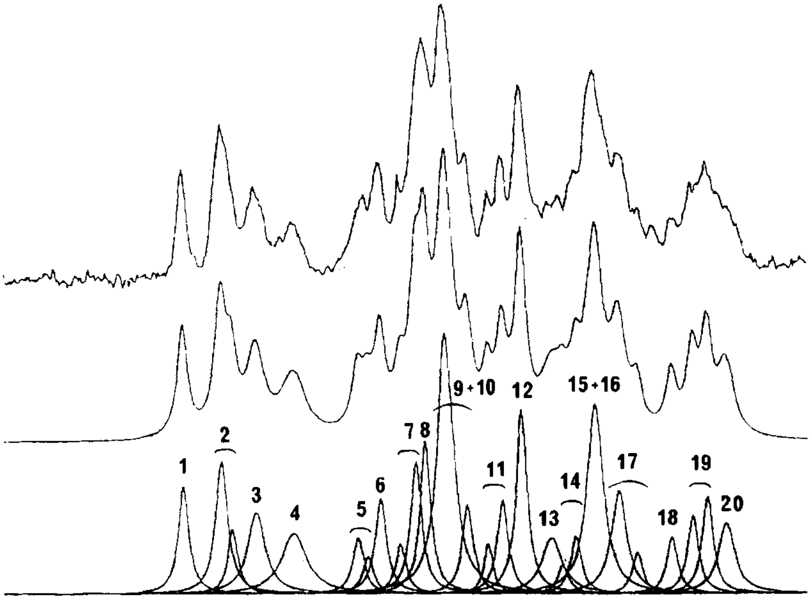


FIGURE 3 Curve deconvolution of the methylene ^{13}C spectral region of sample *a*: top trace, observed spectrum; middle trace, fitted spectrum; lower trace, individual components.

Similarly, we examined the published data of Sato's [23]. Sato's quantitative data were obtained also at a higher temperature (150°C) but at a lower field (50.1 MHz). They divided the ^{13}C methylene resonances into 12 spectral regions. Using our peak numbering and assignment scheme (Table III), these 12 spectral regions can be assigned. The data are then fitted to first-order Markovian models (Table VI). The fits are generally satisfactory, and all three samples follow approximately Bernoullian statistics ($P_{mr} + P_{rm} \approx 1$).

Note that the assignments given above are mostly based on hexads. As noted earlier by Kawamura et al. [31], several hexads show sensitivity to long-range configurations (heptads or octads). For example, from the assignment scheme in Table III, it is obvious that the (mrrrr) hexad is split into two resonances (peaks 5 and 6). Similarly, the (mrmmm) hexad is split into two resonances (peaks 8 and 9). We found evidence for similar splittings at least for the following hexads: (rmmrr), (rmmmr), (mmmmr), (mmmmm), and (mmrrr). The case of (mmmmm) is fairly straightforward: (mm*m*mmm) resonates at 43.62 ppm and (mm*m*mmr) occurs slightly downfield at ~ 43.66 ppm. The fact that splittings are observed for (mrrrr), (mmrrr), and (mmmmr) hexads is intriguing. One possible reason for such splitting is that a string of m units may stiffen the polymer chain, thereby leading to different distributions of isomeric states and different ^{13}C shifts.

In addition to the above hexads, a number of CH_2 resonances are broadened, also suggesting sensitivity to longer range n-ads. For example, the following resonances (at least) are probably sensitive to octads: (mrrrm), (rmrmr), (rmrmm), and (mmrmm). The broadening in the latter three hexads are so severe that in many spectra they show up together as a broad spectral pattern.

TABLE IV

First order Markovian probabilities and the observed versus calculated CH_2 intensities for atactic polystyrene (sample a)

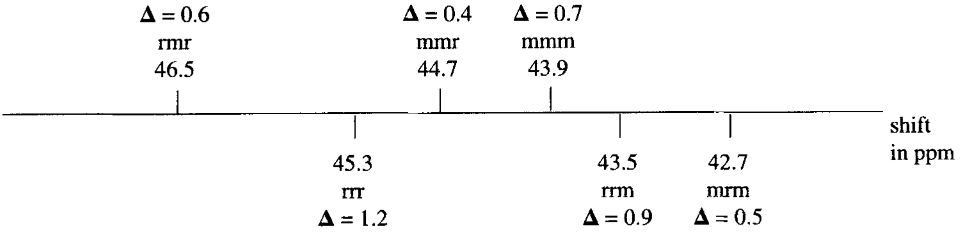
No	^{13}C Shift	Assignment	Probability[a]	Observed[b]	Calculated[c] ($P_m = 0.48$)
1	46.8	mrmrm	$P_{mr}^2 P_{rm}^3$	3.5	3.0
2	46.5	rrmrm	$2 P_{mr}^2 P_{rm}^2 P_{rr}$	7.1	6.5
3	46.2	rrmrr	$P_{mr}^2 P_{rm} P_{rr}^2$	4.6	3.5
4	45.9	mrrrm	$P_{mr} P_{rm}^2 P_{rr}^2$	4.9	3.2
5	45.4	mrrrr	$2P_{mr} P_{rm} P_{rr}^3$	6.6	7.0
6	45.2				
7	44.9	mrmmr	$2 P_{mr}^2 P_{rm}^2 P_{mm}$	11.6	11.5
8	44.8	r (mrmmm) x	$2 P_{mr}^2 P_{rm}^2 P_{mm}^2$		
	44.8	m (mrmmm) x	$2 P_{mr} P_{rm}^2 P_{mm}^3$		
9	44.7	rrrrr, rrmmm	$P_{mr} P_{rr}^4 + 2P_{mr} P_{rm} P_{mm}^2 P_{rr}$	16.4	15.8
	44.6	m (rmmrr) x	$2 P_{mr}^2 P_{rm}^2 P_{mm} P_{rr}$		
10	44.5	r (rmmrr) x	$2 P_{mr}^2 P_{rm} P_{mm} P_{rr}^2$		
11	44.3	rmmmr	$P_{mr}^2 P_{rm} P_{mm}^2$	3.6	3.0
12	44.1	rmrrm	$2 P_{mr}^2 P_{rm}^2 P_{rr}$	7.1	6.5
13	43.8	mmmmr	$2 P_{mr} P_{rm} P_{mm}^3$	2.4	5.5
14	43.7	mmmmm	$P_{rm} P_{mm}^4$	2.2	2.5
15	43.5	rmrrr	$2P_{mr}^2 P_{rm} P_{rr}^2$	11.7	13.0
16	43.4	mmrrm	$2P_{mr} P_{rm}^2 P_{mm} P_{rr}$		
17	43.2	mmrrr	$2 P_{mr} P_{rm} P_{mm} P_{rr}^2$	6.7	6.5
18	42.8	rmrmr	$P_{mr}^3 P_{rm}^2$	2.0	3.2
19	42.7	rmrmm	$2 P_{mr}^2 P_{rm}^2 P_{mm}$	5.9	6.0
20	42.5	mmrmm	$P_{mr} P_{rm}^2 P_{mm}^2$	3.7	2.8

[a] Unnormalized; for normalization, multiply expressions by $(P_{mr} + P_{rm})^{-1}$.

[b] Average of two curve deconvolution efforts.

[c] For Bernoullian model, $P_m = P_{rm} = 1 - P_{mr}$; mean deviation = 0.8.

One way to examine our assignment scheme is to observe the ^{13}C shifts at the tetrad level. Using the presentation diagram devised by Harwood et al. [24], we can summarize our assignments as follows:



Also included in the above presentation is the spread in the ^{13}C shifts due to tacticity splitting at the hexad level (designated Δ). Note that at the tetrad level, our assignment scheme is similar to Harwood's [24].

TABLE V

Analysis of the CH_2 NMR data for two polystyrene samples reported by Kawamura et al. [31], using the revised assignments given herein

No[a]	Revised Assignments[a]	Sample APS		Sample IR-PS	
		I_{obsd}	I_{calc}	I_{obsd}	I_{calc}
1	mrmrm	2.4	2.8	2.4	2.4
2	rrmrm	6.7	6.7	1.9	1.5
3	rrmrr	4.3	4.0	2.3	1.3
4	mrrrm	3.6	3.3		
5 + 6	mrrrr	7.9	7.9		
7 + 8	mrmmr + r(mrmmm)x	8.5	8.2	9.2	8.5
9 + 10	m(mrmmm)x + rrrrr rrmmm + rmmrr	18.9	19.2	19.0	18.8
11 + 12	rmmmr + rmrrm	11.0	9.5	3.7	3.9
13 → 17	mmmmr + mmmmm rmrrr + mmrrm mmrrr	24.4	27.0	49.7	49.8
18 → 20	mrm	12.2	11.4	11.6	13.6
Model fitting					
P_m			0.458		0.769
mean dev.			0.7		0.5

[a] Assignment and peak numbers as given in Table III, except for the m(mrmmm)x octads which (under the experimental conditions used byKawamura) appear to fall under peak 9 (instead of peak 8).

TABLE VI

Reaction probability model calculations on the NMR data published by Sato et al. [23], according to the revised assignment scheme, given herein

No[a]	Sato/BPO		Sato/BuLi		Sato/BF_3	
	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}
1	2.6	2.6	2.4	2.4	3.8	3.2
2	6.4	6.5	6.1	6.6	5.5	5.4
3	4.0	4.0	4.5	4.5	2.6	2.3
4	3.6	3.3	4.0	3.4	2.9	2.8
5 + 6	7.6	8.2	10.1	9.3	4.7	4.7
7	4.3	5.4	5.4	5.0	(6.5)[b]	6.5
8 + 9 +10	21.5	22.3	21.5	22.5	(22.9)[b]	22.6
11 → 13	12.8	14.2	11.3	13.3	12.5	17.1
14 → 17	23.9	22.6	24.6	22.9	24.4	22.3
18	2.7	3.1	2.4	3.2	2.6	2.6
19	6.7	5.4	5.3	5.0	6.5	6.5
20	2.9	2.4	2.3	2.0	5.1	4.1
Model fitting						
P_{mr}		0.536		0.560		0.444
P_{rm}		0.448		0.422		0.540
mean dev.		0.6		0.7		0.8

[a] Assignments and peak numbers as given in Table III.

[b] Sato et al. [23] reported the combined intensities of these two resonances as 29.4 ppm.

According to our assignments, the average shift for the (*m*) configuration is 45.0 ppm and for the (*r*) configuration is 43.8 ppm. The configurations with racemic neighboring units (rxr, where $x = m$ or r) have the most downfield shifts, probably reflecting the decreased steric crowding in these configurations. The presence of one meso neighboring unit (mxr) gives a large upfield shift (viz., rxr − rxm ≈ 1.8 ppm). The presence of two neighboring meso units causes incrementally lesser shifts (viz., mxr − mxm ≈ 0.8 ppm). Thus, the incremental ^{13}C shifts for the tetrads are not additive. No simple additive shift rules apply to the methylene ^{13}C shifts.

Assignment of Methine ^{13}C

An expanded ^{13}C spectrum of the methine region for atactic polystyrene is shown in Figure 4. The assignment of methine carbon has never been ascertained previously. From epimerization results, Harwood et al. [24,26] observed that the isotactic mm-triad occurs at about 0.2 ppm downfield from the other triads; complete assignments were not reported.

Using a similar assignment procedure as we did for the methylene, we were able to assign the methine carbon, as given in Figure 4 and Table VII. The assignments were carried out at the pentad level. Moreover, we can fit the observed intensities of the atactic polystyrene to the assignment scheme. Again, it is necessary to use curve deconvolution to obtain the spectral intensities. The observed spectrum and the fitted components are shown in Figure 5. With the use of the assignment scheme, the intensities of atactic polystyrene (sample *a*) can be readily fitted to a Bernoullian model (with $P_m = 0.48$). The fit (Table VII, last column) is acceptable.

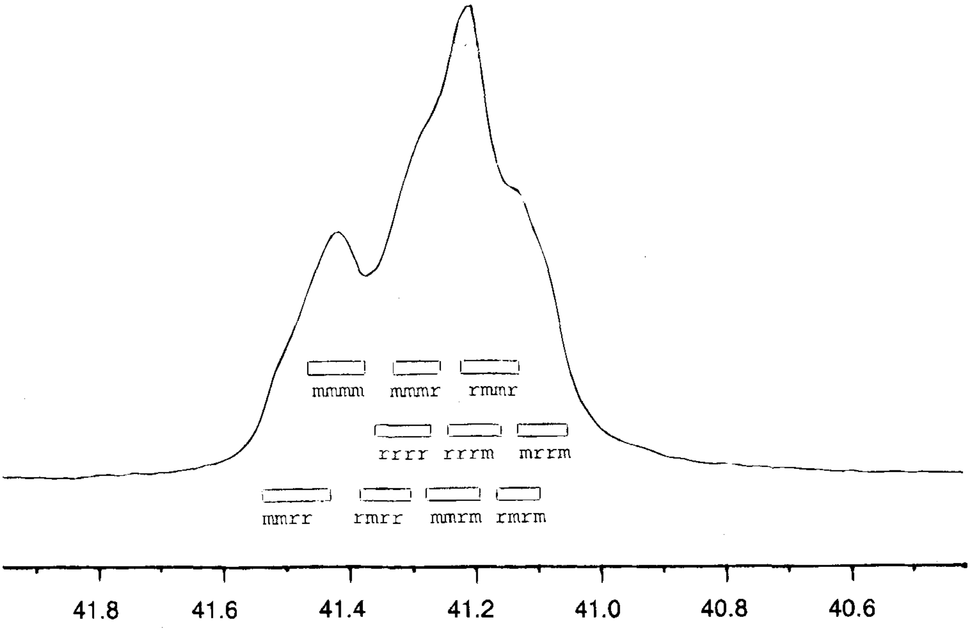


FIGURE 4 ^{13}C NMR spectrum of backbone methine carbon of sample *a* in 1,2,4-trichlorobenzene at ca. 115°C, with assignments shown below the spectrum.

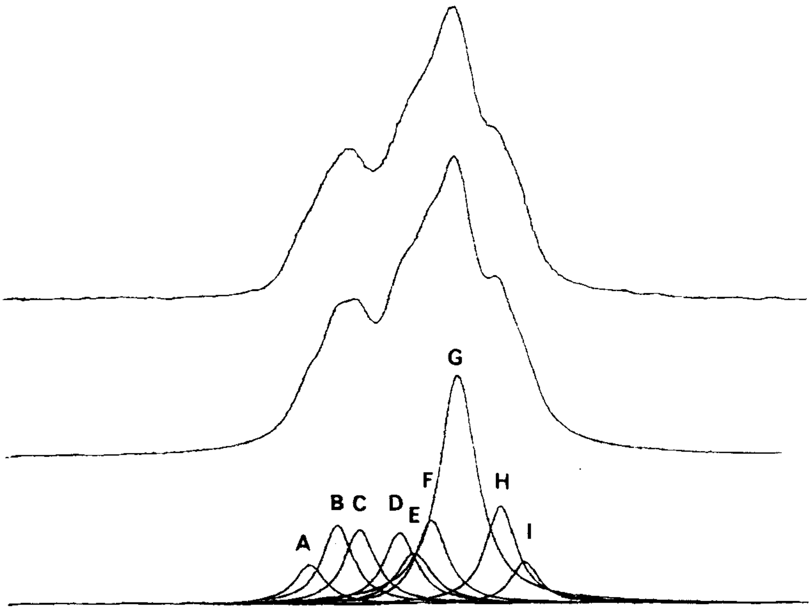


FIGURE 5 Curve deconvolution of the methine ^{13}C region of sample *a*: top trace, observed spectrum; middle trace, fitted spectrum; lower trace, individual components. The letter codes correspond to column 1 of Table VII.

TABLE VII

Spectral assignments and observed versus calculated backbone CH intensities for sample *a*

Code	^{13}C Shift	Assignment	Probability[a]	Observed[b]	Calculated[c] ($P_m = 0.48$)
A	41.49	mmrr	$2kP_{rm}P_{mm}P_{mr}P_{rr}$	14.6	12.5
B	41.43				
C	41.39	mmmm	$kP_{rm}P_{mm}^3 +$	18.2	18.8
D	41.31	rmrr	$2kP_{mr}^2P_{rm}P_{rr}$		
E	41.28	rrrr	$kP_{mr}P_{rr}^3$	7.1	7.3
F	41.25	mmmr	$2kP_{rm}P_{mm}^2P_{mr}$	10.3	11.5
G	41.20	rrrm	$2\,kP_{mr}P_{rr}^2P_{rm} +$	33.2	31.2
		mmrm	$2\,kP_{rm}^2P_{mm}P_{mr} +$		
		rmmr	$kP_{mr}^2P_{rm}P_{mm}$		
H	41.11	rmrm	$2\,kP_{mr}^2P_{rm}^2$	11.9	12.5
I	41.06	mrrm	$kP_{rm}^2\,P_{mr}P_{rr}$	4.5	6.2

[a] $k = (P_{mr} + P_{rm})^{-1}$.

[b] Obtained through curve deconvolution, Figure 5.

[c] Mean deviation = 1.2. In the Bernoullian model, $P_m = P_{xm} = 1 - P_{xr}$ ($x = m$ or r).

Assignments of ^1H NMR spectra

In the 2D ^{13}C-^1H shift-correlated experiment, the ^{13}C shifts are correlated to the shifts of the adjoining ^1H nuclei, thus permitting the assignments of either the ^1H or the ^{13}C spectrum whenever the other is known [35]. The ^{13}C-^1H shift correlation maps (CSCM) for the atactic polystyrene backbone methine and methylene are given in Figure 6. Both the stacked plot (Figure 6a) and the contour plot (Figure 6b) are given. From the plots, it is clear that the methine ^{13}C at ca. 41.5 ppm is correlated with the methine ^{1}H at 1.8–2.4 ppm. Similarly, the methylene ^{13}C at 42–47 ppm is correlated to the methylene ^{1}H at 1.5 ppm.

In the literature, the ^{1}H NMR assignments were mostly carried out on the methines. An expanded 2D plot of the methine region is shown in Figure 7. According to the epimerization results of Shepard et al. [9] and the model polymers of Ishihara et al. [13], the (mm) triad occurs at 2.1 ppm, and the (mr) + (rr) triads at ca. 1.9 ppm in the ^{1}H spectrum. The 2D plot suggests that this is indeed the case, but the (mm) triad also has a small tail that partially extends into the larger resonance that contains the (mr) and (rr) triads.

The ^{1}H methylene region has not been fully assigned previously although it is known that the methylene resonance is shifted to higher fields in the order: isotactic, atactic, and syndiotactic [13]. Full assignments have been difficult because all the tacticity sequences are crowded in a narrow chemical shift range (1.44–1.61 ppm). Furthermore, it has been shown [5,13] that the methylene protons in the (mmm) tetrad are non-equivalent. From structural considerations, we would expect the methylene protons in (mmm), (mmr), (rmr), and (mrr) tetrads to be non-equivalent although the magnitude of the ^{1}H shift difference may vary.

By analogy to the ^{1}H spectrum of polypropylene [36], the two methylene protons on the (mmm) tetrad are expected to have the largest difference in their ^{1}H shifts ($\delta_B - \delta_A$). Heatley and Bovey [5] have calculated the following parameters for isotactic polystyrene at 100°C.

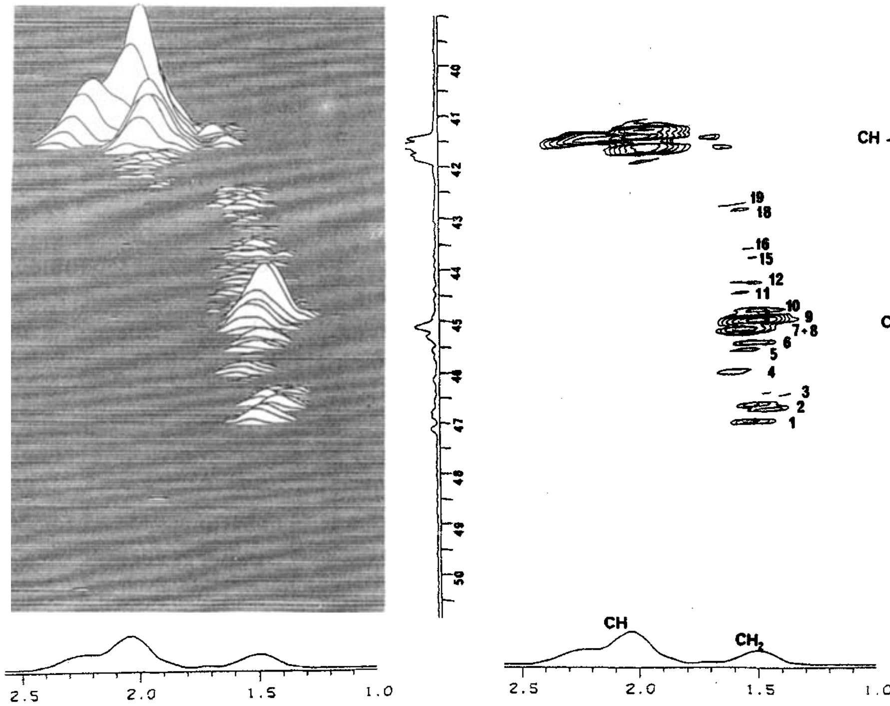


FIGURE 6 2D ^{13}C-^{1}H CSCM plot of atactic polystyrene, sample *a* (methylene and methine region): (a) stacked plot, (b) contour plot. For clarity, selected peak numbers (as given in Table III) have been noted in the contour plot.

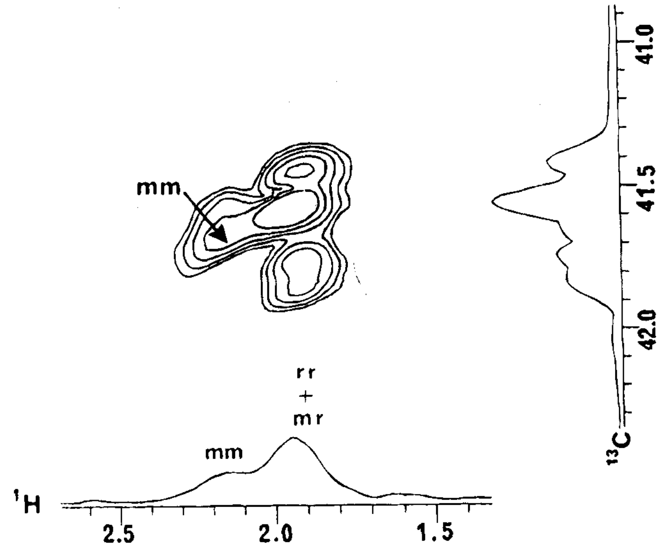
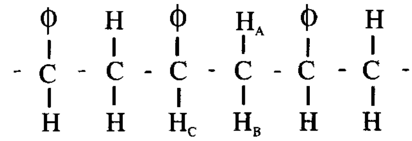


FIGURE 7 2D ^{13}C-^{1}H CSCM plot of atactic polystyrene (methine region only)



$$\begin{array}{ccccccccccccc} & \phi & & H & & \phi & & H_A & & \phi & & H & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & \\ & H & & H & & H_C & & H_B & & H & & H & \end{array}$$

$\delta_A = 1.501$ ppm; $J_{AB} = -14.5$ Hz

$\delta_B = 1.574$ ppm; $J_{AC} = 7.25$ Hz

$\delta_C = 2.229$ ppm; $J_{BC} = 6.25$ Hz

$\delta_B - \delta_A = 0.073$ ppm.

At 300 MHz, $\delta_B - \delta_A = 21.9$ Hz, and a second-order spectrum is expected for the (mmm) tetrad, as was indeed found by Ishihara et al. [13] Since the $\delta_B - \delta_A$ values are expected to be smaller for the (mmr), (rmr), and (mrr) tetrads, they most likely exhibit second-order spectral patterns as well. In the 2D CSCM spectra at 300 MHz (Figure 6a), these patterns contribute to broadened peaks in the ^{1}H dimension.

By taking the center of the ^{1}H peaks (including second-order patterns) and carefully study the 2D plots, we can make tentative ^{1}H assignments, as shown in the second column of Table III.

It appears that the ^{1}H shifts are not only sensitive to tetrads, but also to hexads. The trend in the shifts (isotactic most downfield, syndiotactic most upfield) is only true for pure isotactic and pure syndiotactic polymers. At the tetrad level, a systematic trend is observed for the m-centered tetrad (mmm > mmr > rmr, with increasing field), but less distinct for the r-centered tetrads (mrm > mrr ≈ rrr, with increasing field). At the hexad level, the trends are also not clear-cut. For two tetrads (mmm and mrm), the long-range meso and racemic units have a little or no effect, but the other tetrads are indeed sensitive to long-range configurations. For two tetrads (mrm and rrr), a long-range meso configuration tends to move the ^{13}C shifts downfield (viz., *m*rmr*m* > *m*rmrr > rrmrr, and *m*rrr*m* > *m*rrrr > rrrrr, with increasing field).

In at least two cases (peak 2: rrmrm hexad; and peaks 5 and 6: mrrrr hexad), the data indicate that the ^1H and the ^{13}C shifts are both sensitive to heptads. The fact that the ^1H spectrum can detect such a long-range configurational effect is of interest. Note that the heptad sensitivity of peak 2 (rrmrm hexad) is only apparent in the 2D plot (Figure 6b) and not seen in the normal 1D spectrum.

Spectral Simulation Approach

Thus far in this work, we have used the conventional analytical approach for the NMR analysis of polymers. Thus, we assign the spectrum, obtain the intensities, and carry out model fitting. An alternative method to tackle the problem of polymer microstructure is to start with an appropriate statistical model, generate the polymer sequences (or polymer chains), relate the sequences to ^{13}C shifts, and obtain the simulated spectrum. This is the gist of the computer simulation ("synthetic") approach [37–42].

Statistical model → Reaction probabilities → Model calculations → Predicted sequences → Predicted spectrum & intensities

Earlier, a computer program, called PSPEC, has been written [37] that permits sequence distribution and copolymer ^{13}C NMR spectra to be simulated. A separate program (CAL23) has been designed for ethylene/propylene copolymers,[38] and a related program (CAL33) can simulate the ^{13}C NMR spectrum of polypropylene tacticity and regioirregular structures.[39] In the case of polystyrene tacticity, spectral simulation is more difficult because the relationship between ^{13}C shifts and microstructure is complex. The ^{13}C shifts for methylene, for example, do not exhibit a simple incremental additive relationship with respect to neighboring meso and racemic units. In view of this difficulty, a slightly different mode of computer simulation is carried out.

In this simulation, a statistical model is first chosen from which the conditional probabilities are calculated. On the basis of the spectral assignments, each observed NMR resonance can be associated with a theoretical reaction probability (e.g., Table IV, column 4 for backbone CH_2, and Table VII, column 4 for backbone CH), and the expected intensity calculated from the theoretical reaction probability. We then use the observed ^{13}C shift for each resonance, together with the calculated intensity, to produce a simulated ^{13}C spectrum. The entire process (below) has been coded into a QuickBASIC program called CALSTY [43].

Statistical model → Reaction probabilities → Calculated intensities → Use assigned ^{13}C shift positions → Predicted spectrum

The simulated ^{13}C spectrum of the aliphatic region of atactic polystyrene is shown in Figure 8. A total of 30 resonances (including split hexads, as shown in Table III, column 3) are used. The agreement with the observed spectrum (Figure 2) is satisfactory.

CONCLUSIONS

In this work, we re-visited the polystyrene tacticity problem. For the ^{13}C spectrum, we were able to obtain new assignments for CH and revised assignments for CH_2. Quantitative analysis have been carried out by computer-assisted analytical (model fitting)

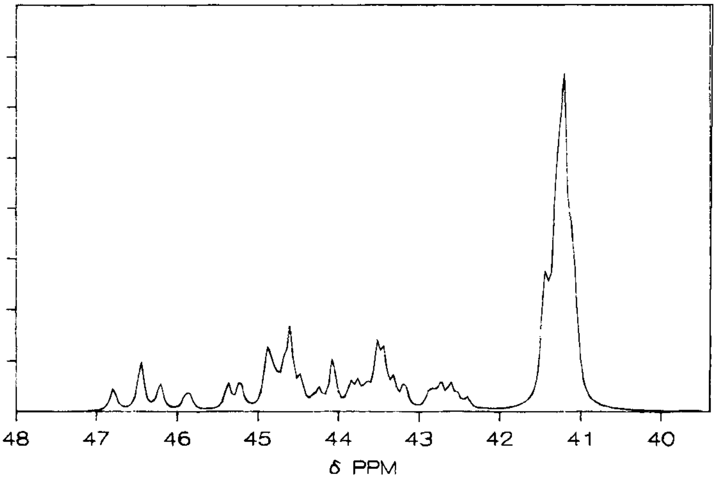


FIGURE 8 Simulated ^{13}C NMR spectrum of the methylene region of atactic polystyrene. Bernoullian model with $P_m = 0.48$. The simulation assumes a spectral frequency of 25 MHz and linebroadening of 2.2 Hz.

approach and spectral simulation (synthetic) approach. 2D NMR has been used in conjunction with ^{1}H NMR assignments.

Acknowledgments

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43. Program CALSTY is available by writing to the corresponding author.