Table I
Line-Width Data for Spin-Labeled PHC as a Function of Temperature

T, °C	A,[a] G	B, G	C, G
60	0.634	0.310	0.015
39	0.670	0.518	0.0
22	0.728	0.574	0.019
1	0.75	0.55	0.10
−26	0.71	0.45	0.16
−49	0.71	0.42	0.21
−74	0.95	1.0	0.16

[a] Fit to $\delta = A + B\mathbf{m} + C\mathbf{m}^2$, where $\mathbf{m}$ is the spectral index number of the line.

alcohol sites successfully labeled (determined by spin concentration measurements). ESR spectra of toluene solutions at 1.5 wt % polymer show a reduced intensity of II relative to I. The reduced label density in PCHS would cause less dimerization and hence the reduced intensity of II to the "normal" three-line nitroxide spectrum. If the spectra were due to different motional domains, one would expect the absence of II in PCHS since it does not have two configurational domains like PHS. Furthermore, the subsequent synthesis of PHS labeled with a compound with markedly less pairing tendency than TEMPYO (oxazolidine oxyl label from the copolymer of 1-hexene with 3–5 mol % 1-hexenyl-5-oxazolidine and then subsequent oxidation of the oxazolidine amine group) showed the complete absence of II, indicating that we are not seeing two different motional domains.

Careful measurements of the ESR line widths, δ, of I in the regions where overlap with II is not severe and subsequent fit to the usual quadratic dependence in the spectral index number, $\mathbf{m}$ ($\delta = A + B\mathbf{m} + C\mathbf{m}^2$), show that the dominant relaxation modes are not the usual rotational modulation of anisotropic g and hyperfine tensor components.[12] For instance, if rotational modulation is the dominant relaxation process, plots of C vs. B from spectra at different temperatures would increase monotonically with B.[13] The results of line-width measurements for PHS in toluene after correction for unresolved proton hyperfine splittings[14] by the method of Bales[15] are given in Table I. In our case, B did not change monotonically with either temperature or the coefficient C, indicating that there was more than one type of relaxation process at work. From previous results in the literature and the experimental evidence in this study, it seems clear that TEMPYO labels can undergo self-association even at dilute label concentrations.

Evidence of the same sideband spectra exists in several published reports of studies using TEMPYO labels.[16-19] In most cases the authors do not comment on the presence of the sidebands; however, in most reports, the radical concentration appears to be sufficiently low to remove any serious complications from radical associations. In one case[16] of spin-labeled poly(ethylene oxide) grafted on silica, the radical concentration is marginally high (about 1×10^{-4} M) and it is possible that the interpretation of the spectra as contributions from two motional domains is incorrect and instead should be viewed as arising from radical pairing. Also, Meurisse et al.[19] reported anomalous line-width behavior for TEMPYO spin probes in liquid crystal polyesters relative to other classes of probes. This too might be indicative of association.

This work has established that in the use of TEMPYO spin labels and probes extreme care must be exercised in eliminating any effects from biradical association.

Acknowledgment. The author thanks Prof. Walter Stockmayer of Dartmouth College, whose wisdom and guidance made these observations possible. NSF Grant DMR 79-13227 provided financial assistance for the project.

Registry No. Carboxy-TEMPYO, 2154-68-9; $(H_2C{=}CH(CH_2)_3CH_3)(H_2C{=}CH(CH_2)_4OH)(SO_2)$ (copolymer), 105502-59-8.

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^{13}C NMR Assignments of the Methylene Carbons in Polypropylene

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Much work has been carried out to elucidate the ^{13}C NMR spectrum of atactic polypropylene.[1,2] The methyl pentads had been firmly assigned by 1975.[3] The methylene carbons were fully analyzed by Zambelli, Locatelli, Provasoli, and Ferro[4] (ZLPF) and by Schilling and Tonelli[5] (ST).

Although the assignments of ZLPF[4] and ST[5] agree for the most part, there are notable differences. Since the publication of the ZLPF and ST papers, there have been occasional efforts to verify the assignments. Suter and Neuenschwander[6] compared the ^{13}C NMR spectrum of epimerized polypropylene to both ZLPF and ST models. Unfortunately, the low magnetic field used (22.6 MHz) did not enable them to clearly distinguish between these models, and reasonably good agreement was found with both models. Cheng and Lee[7] used two-dimensional NMR and from the correlation of ^{1}H and ^{13}C methylene shifts found good agreement with the ST model. Fetters et al.[8] recently studied the ^{13}C NMR spectra of hydrogenated

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Table I
Observed and Calculated Methylene Hexad Intensities

	ST scheme		ZLPF scheme			
line no.	hexad	$I_{\mathrm{theor}}{}^{a}$	hexad	$I_{\mathrm{theor}}{}^{a}$	$I_{\mathrm{obsd}}{}^{b}$	obsd shifts, ppm
1	*mrmrm*	3.32			3.41	47.80
2	*mrmrr*	5.74			6.97	47.68
3	*rrmrr*	2.48			2.28[c]	47.55
4	*mrrrm*	2.87			2.28[c]	47.54
5	*mrrrr*	4.97			5.50	47.32
6	*mrmmr*	6.63			6.37	47.18
7	*rrrrr*	2.15			3.19	47.15
8	*rmmrr*	5.74			7.53[c]	47.08
9	*mrmmm*	7.66			7.53[c]	47.08
10	*rrmmm*	6.63			4.94	46.96
11	*mrrmr*	5.74	*rmmmr*	3.32	4.01	46.80
12	*rmmmr*	3.32	*mrrmr*	5.74	2.88	46.72
13	*rrrmr*	4.97	*rmmmm*	7.66	5.08	46.63
14	*mrrmm*	6.63	*mmmmm*	4.42	6.74[c]	46.58
15	*rmmmm*	7.66	*rrrmr*	4.97	6.74[c]	46.58
16	*mmmmm*	4.42	*mrrmm*	6.63	5.65	46.50
17	*rrrmm*	5.74			5.30	46.33
18	*rmrmr*	2.87			3.73	45.88
19	*rmrmm*	6.63			7.35	45.70
20	*mmrmm*	3.83			2.34	45.52

[a] Calculated on the basis of the Bernoullian model, $P_m = 0.536$. [b] From curve deconvolution, Figure 2. [c] Overlapped resonances; intensities equally distributed.

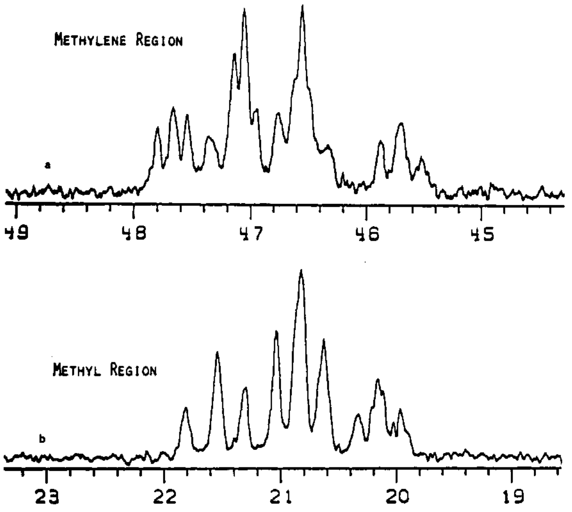

Figure 1. ^{13}C NMR spectrum of atactic polypropylene: (a) methylene region; (b) methyl region.

poly(2-methyl-1,3-pentadiene), but no attempt has been made to compare the assignments of ST or ZLPF.

In our recent studies[9] of polypropylene, we have reexamined the ^{13}C NMR spectra of several atactic polypropylene samples at 75 MHz. The methyl and the methylene regions of a typical sample are shown in Figure 1. From the methyl region, the polymers can be shown to obey Bernoullian statistics with $P_m = 0.536$.

Analysis of the methylene region is not straightforward because of the overlap of the resonances corresponding to different sequences. In this case we used curve deconvolution to separate the various resonances. The observed and the deconvoluted spectra are shown in Figure 2. The intensities for the 20 hexads derived from curve deconvolution are summarized in the sixth column of Table I. Also shown in Table I are the hexad assignments of ST[5] and ZLPF.[4] The theoretical intensities calculated for a Bernoullian polymer with $P_m = 0.536$ in the ST and the ZLPF models are also included.

It appears from Table I that the ST assignments show considerably better agreement with the observed data. This result, together with the earlier two-dimensional NMR work,[7] confirms the correctness of the ST model. In some published spectra,[6,8] the spectral regions corresponding to peaks 6–9 and peaks 13–16 appear congested. For future reference, the ^{13}C shifts observed in this work (at 120 °C) are given in the last column of Table I. The exact assignments (by line number) are also indicated below the x axis in Figure 2c.

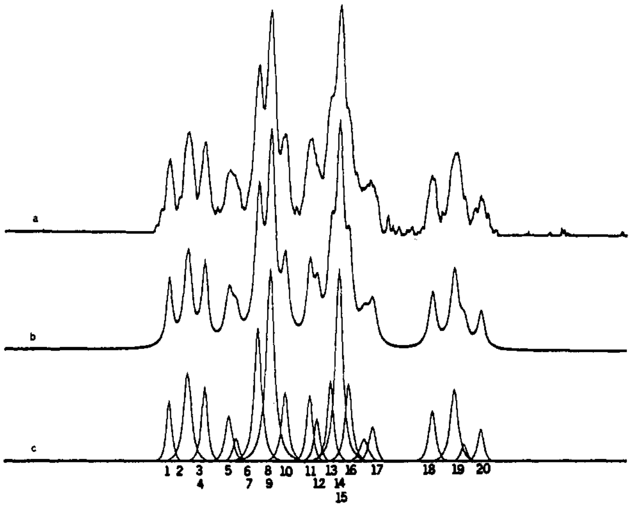

Figure 2. Curve deconvolution of methylene region of polypropylene: (a) observed spectrum; (b) simulated spectrum; (c) individual resonances in the simulated spectrum. The numbering corresponds to peak numbers in Table I.

Experimental Section

The polymer samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 20 wt % with benzene-d_6 added as the field/frequency lock material. The ^{13}C spectra were obtained on a GE/Nicolet NT-300 spectrometer operating at 75.46 MHz. The experimental conditions used were as follows: ^{1}H decoupling, 12-s pulse delay, 1.48-s acquisition time, ±2762-Hz window (with quadrature detection), 16K memory, and 120 °C probe temperature. All ^{13}C shifts were referenced to tetramethylsilane at 0 ppm.

Registry No. Atactic polypropylene, 9003-07-0.

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Dynamic Monte Carlo Study of the Conformational Properties of Long Flexible Polymers

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In this paper we present results of Monte Carlo (MC) studies of long-chain polymers confined to a diamond lattice in which both repulsive and attractive interactions have been included. The hard-core repulsive part of the segment–segment interaction is modeled by the exclusion of multiple occupancy of lattice sites. Attractive interactions, ϵ_a, are associated with every pair of nonbonded nearest-neighbor segments. No preference for any of the three possible (one trans, t, and two gauche, g) rotational states of every internal bond is assumed. Thus the chain stiffness results only from lattice restrictions. The polymer occupies n lattice vertices, connected by $n - 1$ bonds; $n - 3$ conformational states define the chain conformation.

A dynamic sampling method has been used, incorporating reptation type and 3-bond kink motions of the chain backbone, together with 2-bond random flips of the chain ends. The details of the sampling procedure are similar to those in ref 1. We performed simulations on chains of length n = 100, 200, 400, and 800. The reduced temperature $T^* = k_BT/\epsilon_a$ was varied from infinity [the case of an athermal self-avoiding walk (SAW)] to unity, which is well below both the Θ-point and the collapse transition. At a given T^*, $(2–6) \times 10^6$ $[(1.5–4.5) \times 10^7]$ iterations (one attempt at a reptation step plus several attempts at kink flips) have been performed for chains of n = 100 [800]. Depending on n, the conformation of the polymer has been analyzed every 100–1000 cycles of the MC algorithm. Hence from 2×10^4 to 6×10^4 relatively independent "measurements" contributed to the ensemble averages, which were calculated as the appropriately weighted arithmetic mean of the quantity of interest. For some sets of the model parameters (n, T^*), the standard deviations from the mean have been evaluated on the basis of runs obtained with different streams of pseudo random numbers.

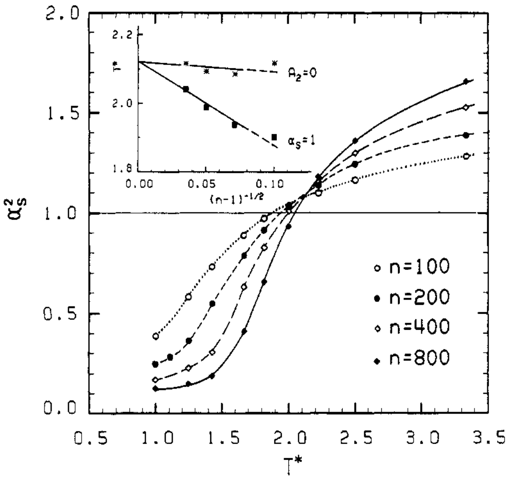

Figure 1. Plot of the expansion factor α_s^2 vs. reduced temperature T^* for various chain lengths. The inset shows the extrapolation to infinite chain length of the temperature at which the second virial coefficient $A_2 = 0$ and the temperature where $\alpha_s^2 = 1$.

The results are presented in Table I, where the mean-square end-to-end distance (radius of gyration) $\langle R^2\rangle$, ($\langle S^2\rangle$), the average number of polymer nearest-neighbor pairs per bead (no contacts down the backbone are considered) $\langle \nu\rangle$, and the average fraction of gauche states per degree of rotational freedom $\langle f_g\rangle$ have been listed vs. T^{*-1}. The second column of Table I contains the number of iterations in the MC process.

The dimensions of the athermal SAW's are fit very well by the relation $\langle R^2\rangle \sim \langle S^2\rangle \sim (n-1)^{1.186\pm0.004}$, in good agreement with previous work.[2,3] As the temperature decreases, the chain dimensions decrease and the number of nearest neighbors increases. The fraction of gauche states also increases slightly, approaching in the high-density state values somewhat greater than the ideal chain $\langle f_g\rangle$ of $^2/_3$. One should note that even the local properties, i.e., $\langle f_g\rangle$ and $\langle \nu\rangle$, are chain-length dependent over the range of n under consideration. While $\langle f_g\rangle$ is weakly n dependent over the entire range of temperature, $\langle \nu\rangle$ depends much more strongly on chain length especially in the low-temperature region (globular state), probably reflecting surface effects.

The expansion factor $\alpha_s^2 = \langle S^2\rangle/\langle S^2_0\rangle$ vs. T^* is presented in Figure 1 for various chain lengths. $\langle S^2_0\rangle$ has been calculated for a finite length n by employing the RIS model with discrete independent rotational states[4] (a nonreversing random walk on a diamond latice). As seen in Figure 1, the Θ-temperature Θ_S, defined as that when $\alpha_s^2 = 1$, varies with chain length. Applying Sanchez's mean field theory (eq 52a of ref 5) to the MC data, we found that it fits our data very well in the vicinity of the Θ-point ($\pm\Delta\epsilon_a/k_BT \simeq 0.1$) when the chain length is rescaled by the persistence length (which is about 3.2 bond lengths). A slightly better fit in the vicinity of the Θ-point was found by using the renormalization group approach of Duplantier, Jannink, and des Cloizeaux (DJC),[6] giving some evidence for a tricritical state of polymers near the Θ-state. However the value of y (the three-body term) (see eq 3 of ref 6) is found to be 0.066, an order of magnitude larger than was reported in ref 6. Both approaches also enabled us to obtain Θ_A, the temperature where the second virial coefficient vanishes. For finite chains, Θ_S and Θ_A are different, with Θ_A far less dependent on molecular weight. The dimensions of the finite length coil at Θ_A are noticeably greater than those for an ideal chain, i.e., $\alpha_s^2 > 1$. As shown in the inset of Figure 1, both estimates of the Θ-temperature coincide in the limit that $n = \infty$, consistent

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0024-9297/87/2220-0438$01.50/0