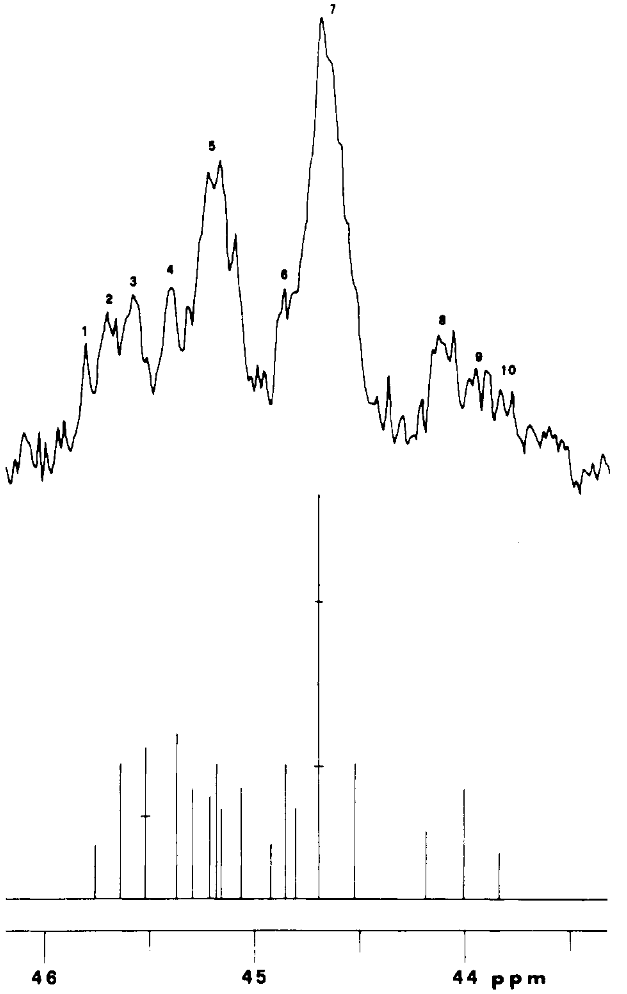

Figure 3. Comparison between the observed and calculated methylene ^{13}C NMR spectra of polypropylene a at 140 °C.

are reasonably well reproduced by the calculation, which however predicts a somewhat wider band than is actually observed; it is possible that errors of the same amount may affect also the other two *r*-centered bands.

On the opposite side of the spectrum we note that the calculation reproduces the *rmr* band quite well. Less clear-cut is the interpretation of the central part of the spectrum, due to considerable overlaps of the peaks. However the overall agreement between calculated and measured intensities seems satisfactory.

Similar considerations are also valid in the case of polymer a (see Figure 3), notwithstanding the poorer quality of the spectrum. Here we note that the *mmmmr* resonance has been assigned of necessity to peak 7, although on the sole grounds of the calculated chemical shift it could be assigned to peak 6. Moreover the relative intensities of the *mrm* band are not as adequately reproduced as those for polymer s.

Considering also the different tacticity of the two polymer samples examined, we may conclude that the present work provides a significant advance in the interpretation of the methylene region of polypropylene spectra. More in general, this work shows that the information derived from observations on model compounds may be fruitfully coupled with the current semiempirical methods for understanding ^{13}C NMR spectra of polymers.

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Carbon-13 Nuclear Magnetic Resonance of Atactic Polypropylene

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ABSTRACT: ^{13}C NMR spectra were recorded at 90.52 MHz for a low molecular weight atactic polypropylene dissolved in a variety of solvents over a broad temperature range (20–120 °C). Comparison of chemical shifts calculated via the γ effect method with the observed resonances, whose relative chemical shifts are solvent independent, permitted their assignment to most of the methyl heptad, methylene hexad, and methine pentad stereosequences. Agreement between observed and calculated chemical shifts required γ effects, i.e., upfield chemical shifts produced by a gauche arrangement of carbon atoms separated by three bonds, of ca. −5 ppm for the methyl and methine carbons and ca. −4 ppm for the methylene carbons. Comparison of the observed and calculated intensities of the assigned resonances indicated that neither Bernoullian nor first-order Markovian statistics describe the polymerization mechanism of the polypropylene sample under study.

We have recently been interested in the ^{13}C NMR chemical shifts of vinyl homo- and copolymers.[1-8] Quantitative accounting of the number of gauche arrangements involving a given carbon atom with other carbons three bonds removed (γ carbons) permits the calculation of its ^{13}C chemical shift. Such a three-bond gauche arrangement of carbons produces an upfield chemical shift, or γ effect,[1,2,9-12] of ca. −5 ppm relative to their trans arrangement.

Application of the γ effect method of calculating ^{13}C chemical shifts has achieved agreement between the observed and predicted chemical shifts of the carbons in polypropylene model compounds,[3,6] ethylene–propylene

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copolymers,[4,8] poly(vinyl chloride)[5] and its oligomers, and polystyrene oligomers.[7] In this report we describe our attempts to assign the ^{13}C NMR spectra of atactic polypropylene by comparison of observed and calculated chemical shifts.

We were encouraged in our attempt to assign the ^{13}C NMR spectra of atactic polypropylene by our successful prediction[3] of the observed chemical shifts of the 9-methyl carbon in the various stereoisomers of 3,5,7,9,11,13,15-heptamethylheptadecane (HMHD). Zambelli and coworkers[13-15] synthesized 12 of the isomers of HMHD, which are excellent model compounds for the various stereosequences in polypropylene, with ^{13}C enrichement of $(CH_3)_9$. They observed their ^{13}C NMR spectra in 1,2,4-trichlorobenzene at 20, 80, and 140 °C and reported the chemical shifts of $(CH_3)_9$ in each of the isomers.

The Suter–Flory[16] rotational isomeric states (RIS) model of polypropylene was used to calculate the conformational probabilities of bonds 8 and 9 on either side of the backbone from $(CH_3)_9$. From the bond conformational probabilities, the number of three-bond gauche arrangements of $(CH_3)_9$ with $(CH)_7$ and $(CH)_{11}$ was determined for each HMHD isomer. Each such gauche arrangement, or γ effect, was assumed to result in an upfield chemical shift of -5.3 ppm.

The ^{13}C NMR chemical shifts calculated[3] in this fashion were found to be in excellent agreement with the chemical shifts exhibited by the 12 isomers of HMHD synthesized and observed by Zambelli et al.[13-15] Chemical shifts calculated for HMHD via the γ effect method also correctly describe the temperature dependencies of the observed chemical shifts from T = 20–140 °C. Additional chemical shifts were calculated for the $(CH)_9$ methine and $(CH_2)_8$ and $(CH_2)_{10}$ methylene carbon atoms in the HMHD isomers, but there are no experimentally observed chemical shifts available for comparison.

In an attempt to assign all of the observed resonances in the ^{13}C NMR spectra of atactic polypropylene[17,18] to their constituent stereosequences, we calculated the ^{13}C chemical shifts expected for all methyl heptads, methylene hexads, and methine pentads via the γ effect method. ^{13}C NMR spectra are recorded at 90.52 MHz on a low molecular weight sample of atactic polypropylene in order to provide solubility in a variety of solvents (cf. seq.) and over a range of temperatures. Comparison of observed and calculated chemical shifts permits assignment of virtually all observed resonances and enables us to test various statistical models of chain propagation during polymerization of polypropylene.

Experimental Section

Materials. The atactic polypropylene employed was Epolene X-3259-11B, which was manufactured by Eastman Chemical Products, Inc. From vapor pressure osmometry it was determined to have a $\bar{M}_n$ = 2560, corresponding to DP = 61. Prior to the NMR measurements, the polymer was dissolved in 1,2,4-trichlorobenzene and reprecipitated in cold methanol. The material was then dried at room temperature under vacuum for 25 h. Our ^{13}C NMR spectra did not exhibit any evidence of chain branching or head-to-head tail-to-tail monomer insertion in this polymer.

^{13}C NMR Measurements. The NMR spectra were recorded on a Bruker HX-360 spectrometer with a carbon frequency of 90.52 MHz. In all measurements broad band noise decoupling was used to decouple protons from carbon nuclei, the pulse angle was 90°, and the free induction decays were stored in 32K computer locations, using a spectral window of 18181 Hz. Hexamethyldisiloxane (HMDS) was used as an internal reference (2.0 ppm vs. Me_4Si). Polymer samples were observed as 20% (w/v) solutions. For the solvents heptane and CCl_4, an external capillary of D_2O was used to lock the spectrometer. For the solvents C_6D_6, $CDCl_3$, and 1,2,4-trichlorobenzene–p-dioxane-d_8 the internal deuterium signal was employed. In the solvent mixture, TCB–p-dioxane-d_8, a 3:1 ratio of the two solvents was used. Temperatures were measured with a calibrated thermocouple and a thermometer placed in a tube of ethylene glycol. Depending on the temperature, between 700 and 5000 scans were required for each spectrum. A delay time of 3.0 s was used between pulses.

Based on the work of Freeman and Hill,[19] it is possible to obtain quantitative data from spectra obtained with a pulse delay of less than three T_1. The T_1 values for each carbon must be known for the experimental conditions chosen. The intensities of the different carbons can be related by knowing what percent of maximum intensity is obtained at the pulse delay employed.[20] We have used this technique in obtaining spectra for polypropylene and polyethylene at pulse delays varying from $1T_1$ to $> 5T_1$ and find good agreement in the quantitative results obtained at the different delay times.

Randall[21] has reported T_1 values for the carbons in polypropylene and found a dependence of T_1 on the stereosequence. The largest difference in T_1 values as a result of the stereosequence is the 32% difference between the isotactic and syndiotactic sequences of the methine carbon. Considering our repetition time of 3.0 s and the relaxation data reported by Randall for the three types of carbon in the various stereosequences, we find that the largest intensity errors among stereosequences in our spectra due to nonequilibrium relaxation times would be about 10%. This possible intensity difference was taken into consideration when evaluating various polymerization statistics. The additional factor is not nearly large enough to explain the disagreement between our experimental values and the calculated values for the Bernoullian or first-order Markov models.

Calculation of ^{13}C NMR Chemical Shifts

^{13}C NMR chemical shifts were calculated for all 36 methyl carbon heptad, 20 methylene carbon hexad, and 10 methine carbon pentad stereosequences, using the Suter–Flory[16] RIS model of polypropylene conformations as described in ref 3. The three-bond gauche or γ effects of methine carbons on methyl carbons and methylene and methyl carbons on methine carbons ($\gamma_{CH_3,CH}$, $\gamma_{CH,CH_2 \text{ and } CH_3}$) were taken to be -5.3 ppm upfield relative to their trans arrangements, based on our study[3] of the isomers of HMHD. The γ effect of methine carbons on methylene carbons ($\gamma_{CH_2,CH}$) was reduced to -3.7 ppm, because the overall observed spread of the chemical shifts in the methylene region of the ^{13}C NMR spectra of our atactic polypropylene is reproduced by $\gamma_{CH_2,CH} = -3.7$ ppm (cf. seq.).

Chemical shifts were calculated at 20, 80, and 140 °C, and values corresponding to intermediate temperatures were obtained by interpolation. Only relative ^{13}C chemical shifts were obtained, and no attempt was made to derive the intrinsic chemical shift expected for each carbon type[2,9-11,18,24,25] in the absence of γ effects.

Results and Discussion

Tables I–III present the calculated and observed chemical shifts of the methyl carbons at the heptad level, the methylene carbons at the hexad level, and the methine carbons at the pentad level. The observed spectra are presented in Figure 1–3, where examples of the effects of temperature and solvent on the ^{13}C chemical shifts are illustrated.

At a given temperature the pattern of ^{13}C NMR resonances in each of the three regions of the spectra appears insensitive to solvent. This solvent independence of relative chemical shifts is even observed in the methylene regions of our polypropylene spectra,[22] a region of the ^{13}C spectrum which can be very markedly influenced by solvent as observed in other vinyl polymers, such as poly(vinyl chloride)[5] and polystyrene.[7] Clearly it is important to know if observed chemical shifts are sensitive to solvent environment when making resonance assignments by com-

Table I
Calculated and Observed ^{13}C Chemical Shifts for the Methyl Carbon Atoms in the Stereoisomers of Polypropylene

	42 °C		118 °C	
stereoisomer	calcd	obsd[a]	calcd	obsd[a]
mmmmmm	0.000	0.00	0.000	0.00
mmmmmr	−0.074	−0.08	−0.048	
rmmmmr	−0.175		−0.110	
mmmmrr	−0.273		−0.223	
mmmmrm	−0.320	−0.41	−0.258	
rmmmrr	−0.377	−0.48	−0.285	−0.28
mrmmmr	−0.422		−0.319	
rrmmrr	−0.565		−0.449	
mrmmrr	−0.635		−0.498	−0.53
mrmmrm	−0.686		−0.531	
mmmrrm	−0.682		−0.717	
mmmrrr	−0.715		−0.742	
rmmrrm	−0.796	−0.82	−0.782	−0.81
rrrmmr	−0.823	−0.90	−0.804	
mmmrmr	−0.835		−0.858	
mmmrmm	−0.871		−0.886	
rmrmmr	−0.956		−0.924	
mmrmmr	−0.989		−0.951	
rrmrrm	−1.009		−0.952	
rrrmrr	−1.063		−0.988	
mrmrrm	−1.089	−1.17	−1.001	−1.03
rrrmrm	−1.123		−1.026	
rrmrmr	−1.184		−1.099	
mmrmrr	−1.247		−1.140	
mrmrmr	−1.271	−1.33	−1.150	−1.17
mmrmrm	−1.313		−1.179	
mrrrrm	−1.543		−1.503	
rrrrrm	−1.608	−1.64	−1.543	
rrrrrr	−1.658	−1.69	−1.573	−1.54
rmrrrm	−1.770	−1.87	−1.674	−1.69
rrrrmr	−1.884		−1.716	
mmrrrm	−1.852		−1.720	
rrrrmm	−1.905	−1.97	−1.751	−1.75
rmrrmr	−2.029	−2.08	−1.854	−1.84
rmrrmm	−2.123	−2.22	−1.904	−1.91
mmrrmm	−2.194	−2.33	−1.943	−1.99

[a] For the purpose of comparing observed chemical shifts to calculated values, all observed values are expressed relative to the most downfield stereoisomer which is set to 0.00 ppm. 1,2,4-Trichlorobenzene-*p*-dioxane-d_8 is the solvent.

Table II
Calculated and Observed ^{13}C Chemical Shifts for the Methylene Carbon Atoms in the Stereoisomers of Polypropylene

	42 °C		118 °C	
stereoisomer	calcd	obsd[a]	calcd	obsd[a]
mrmrm	0.000	0.00	0.000	0.00
rrmrm	−0.098		−0.080	
rrmrr	−0.283	−0.22	−0.215	−0.14
mrrrm	−0.315	−0.39	−0.273	−0.26
rrrrm	−0.531	−0.55	−0.424	−0.45
mrmmr	−0.626		−0.551	
rrmmr	−0.732	−0.80	−0.645	−0.61
rrrrr	−0.810	−0.88	−0.606	−0.65
mrmmm	−0.837	−0.93	−0.695	−0.72
rrmmm	−0.943	−1.15	−0.788	−0.82
mrrmr	−1.094		−0.944	−1.00
rmmmr	−1.133	−1.32	−1.044	−1.07
rrrmr	−1.413		−1.146	
mrrmm	−1.442	−1.48	−1.158	−1.19
rmmmm	−1.396		−1.224	
mmmmm	−1.487	−1.62	−1.306	−1.28
rrrmm	−1.754	−1.87	−1.349	−1.39
rmrmr	−2.066		−1.717	
rmrmm	−2.377	−2.42	−1.914	−1.89
mmrmm	−2.617	−2.77	−2.073	−2.07

[a] For the purpose of comparing observed chemical shifts to calculated values, all observed values are expressed relative to the most downfield stereoisomer which is set to 0.00 ppm. 1,2,4-Trichlorobenzene-*p*-dioxane-d_8 is the solvent.

Table III
Calculated and Observed ^{13}C Chemical Shifts for the Methine Carbon Atoms in the Stereoisomers of Polypropylene

	42 °C		118 °C	
stereoisomer	calcd	obsd[a]	calcd	obsd[a]
mmmm	0.000	0.00	0.000	0.00
mmmr	−0.089		−0.072	−0.05
rmmr	−0.148		−0.118	
mmrr	−0.259	−0.11	−0.279	−0.22
rmrr	−0.280		−0.297	−0.27
mrmm	−0.325		−0.349	−0.33
rmrm	−0.332	−0.34	−0.355	−0.36
rrrr	−0.327		−0.374	
mrrr	−0.355	−0.44	−0.413	−0.46
mrrm	−0.377		−0.455	

[a] For the purpose of comparing observed chemical shifts to calculated values, all observed values are expressed relative to the most downfield stereoisomer which is set to 0.00 ppm. 1,2,4-Trichlorobenzene-*p*-dioxane-d_8 is the solvent.

parison with calculated chemical shifts which are assumed to be unaffected by solvent.

The low molecular weight of our atactic polypropylene sample permitted the recording of ^{13}C NMR spectra in a variety of solvents at the same temperature. To determine the effect of solvent on the ^{13}C chemical shifts, the temperature must be maintained constant, because temperature effects alone in any given solvent can change the appearance of the spectra [see Figure 1b, c].

In part a of Figure 1 the methyl region of the ^{13}C NMR spectrum observed in heptane at 67 °C is compared with a line spectrum corresponding to the ^{13}C chemical shifts calculated at the same temperature for all 36 heptads. The correspondence between calculated chemical shifts and observed resonance positions is excellent, permitting the assignment of resonances listed in Table I.

These assignments receive confirmation from the agreement between the predicted and observed temperature dependence of the methyl region of our spectra. As an example, the resonances assigned to the (*rmmr*) and (*mmrr*) centered heptads are observed to overlap as the temperature is lowered [see Figure 1b, c] in agreement with their calculated chemical shifts, which predict *m*(*rmmr*)*r* and *m*(*rmmr*)*m* heptads (lines 9 and 10) to overlap with the *m*(*mmrr*)*m* and *m*(*mmrr*)*r* heptads (lines 11 and 12) somewhere below 67 °C (see Table I).

Integration of methyl heptad resonances and utilization of the relationships[23] connecting hexad and heptad intensities, e.g., (*mmmmm*) = (*mmmmmm*) + $^1/_2$(*mmmmmr*), permits us to estimate the intensities of the methylene hexad resonances. The line spectrum calculated at 67 °C for the methylene carbon hexads [see Figure 2a] reflects these intensity estimates. With one or two minor exceptions, both the calculated intensities and the chemical shifts agree with the observed methylene resonances.

The high-field triplet of resonances observed in the methylene region of our spectra [see Figure 2c] which are assigned to the three hexads corresponding to the (*mrm*) tetrad were not observed by Randall[17] in his ^{13}C NMR investigation of atactic polypropylene. This triplet of resonances well removed to higher fields is nicely predicted by the chemical shifts calculated for the *rmrmr*, *mmrmr*, and *mmrmm* methylene hexads, i.e., lines 18, 19, and 20. Sensitivity to octad stereosequences is probably responsible for the broadness of these well-separated hexad resonances

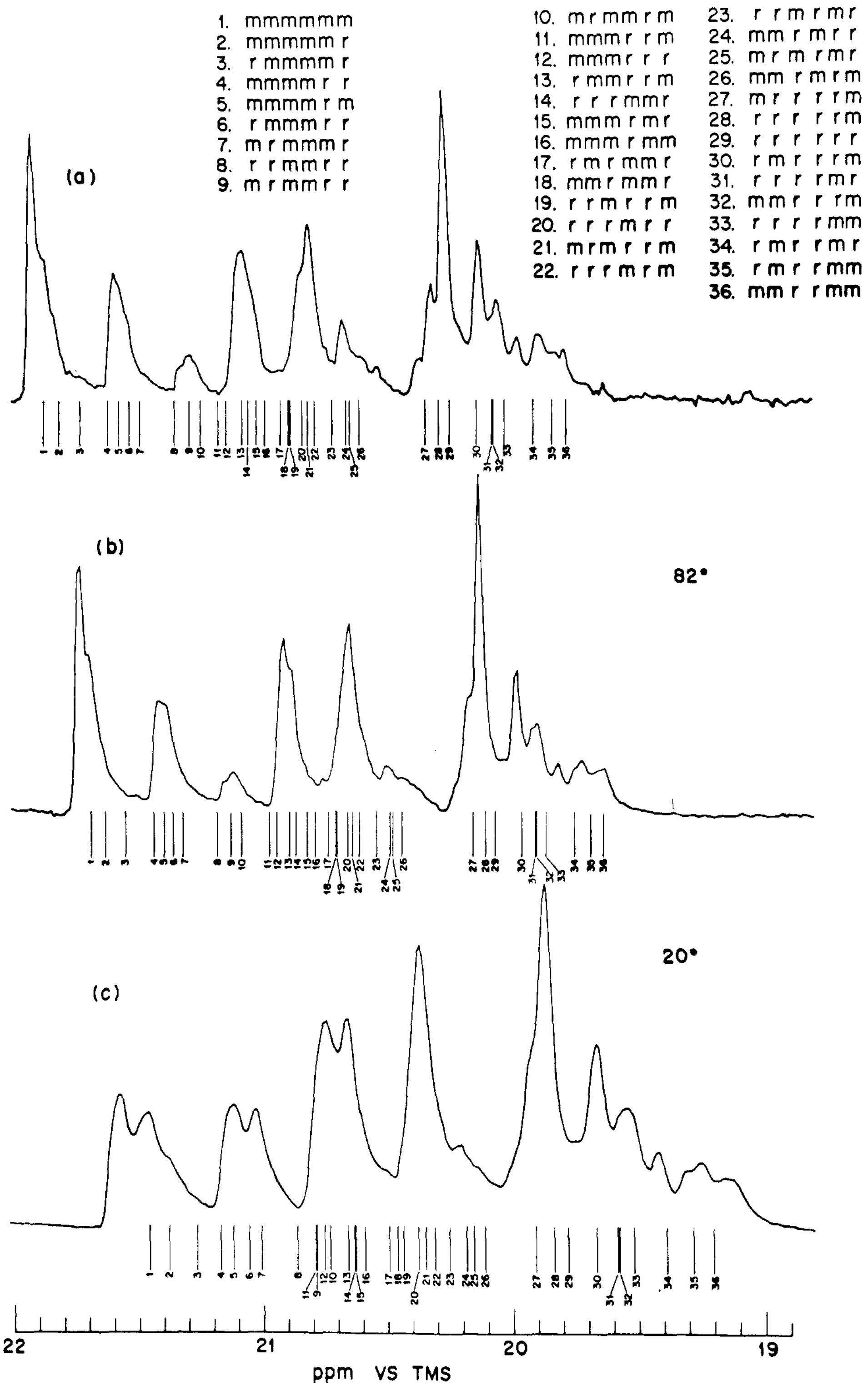

Figure 1. Methyl carbon regions of the ^{13}C NMR spectra of atactic polypropylene recorded at 90.52 MHz. A line spectrum calculated to the heptad level at the temperature of observation appears below each observed spectrum: (a) *n*-heptane at 67 °C; (b) 1,2,4-trichlorobenzene–*p*-dioxane-d_8 at 82 °C; and (c) 1,2,4-trichlorobenzene–*p*-dioxane-d_8 at 20 °C.

and can make their detection difficult.

Integration over all the methyl heptads centered around common pentads leads to an estimate of the methine carbon pentad intensities. Estimated pentad intensities are indicated in the line spectrum calculated at 67 °C for the methine carbons [Figure 3b] by the relative heights of the ten pentad lines. There is good agreement between the calculated and observed pentad resonance positions and intensities. Furthermore, the observed expansion of the methine region with increasing temperatures is faithfully reproduced by the calculated chemical shifts (see Table III).

Once we assigned the methyl, methylene, and methine resonances in the ^{13}C NMR spectra of atactic polypropylene, the estimated intensities of the resonances in each region of our spectra enable us to test the applicability of various polymerization statistics to our sample of polypropylene. From the intensity of the methine (*mmmm*) pentad resonance, a value of $P_m = 0.65$ is derived assuming Bernoullian propagation statistics.[23] This value of P_m leads

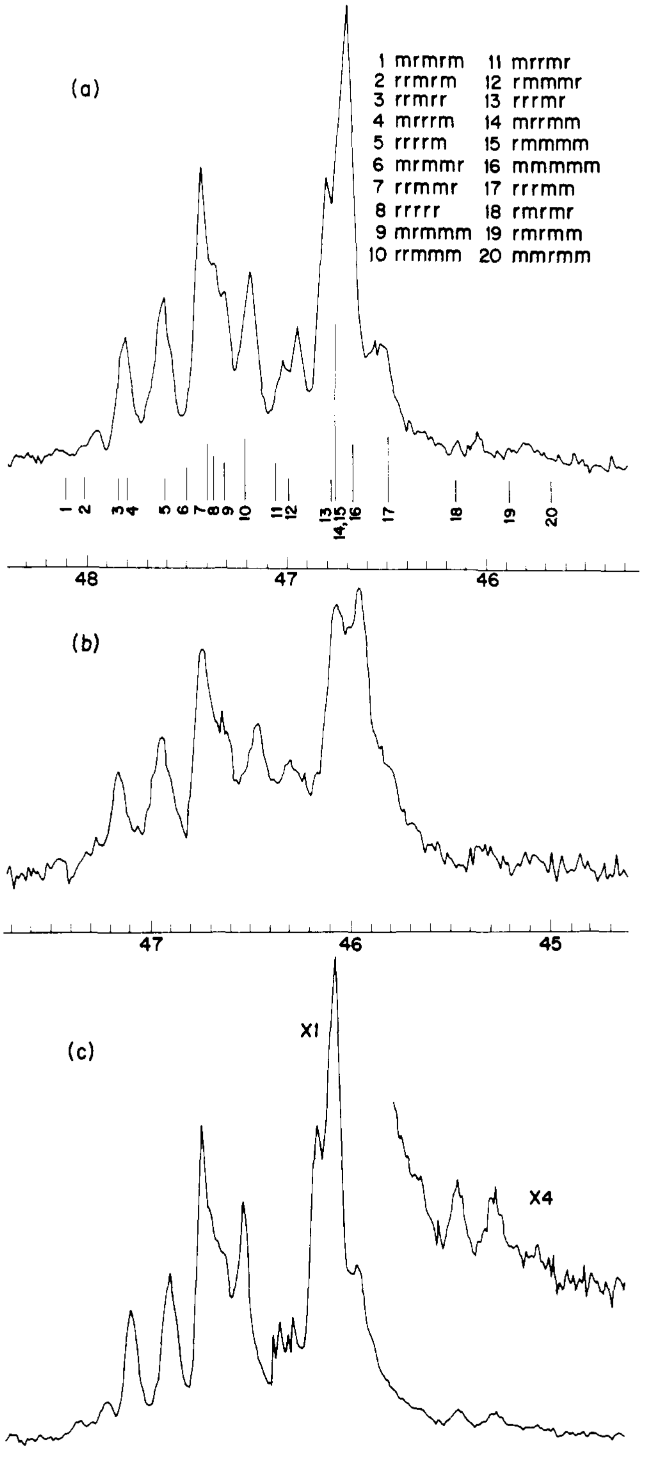

Figure 2. Methylene carbon regions of the ^{13}C NMR spectra of atactic polypropylene recorded at 90.52 MHz: (a) *n*-heptane at 67 °C (a line spectrum also calculated at 67 °C to the hexad level appears below; line heights indicating relative intensities were obtained by integration of the methyl heptad resonances of the spectrum in Figure 1a); (b) CCl_4 at 67 °C; and (c) 1,2,4-trichlorobenzene-*p*-dioxane-d_8 at 118 °C.

to the calculated line spectrum shown in Figure 3c which differs markedly from the observed spectrum.

If instead we use the intensity of the (*rrrr*) methine pentad resonance to obtain P_m ($P_m = 1 - P_r$), a value of 0.33 is obtained. Because the intensities of the methine (*mmmm*) and (*rrrr*) pentad resonances lead to considerably different values of P_m (0.65 vs. 0.33), our sample of atactic polypropylene is clearly not a Bernoullian polymer.

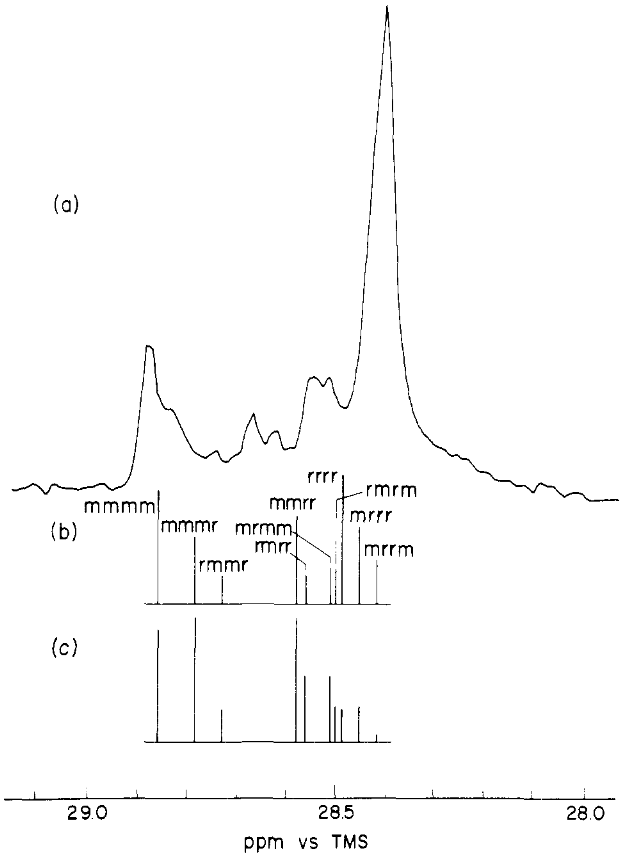

Figure 3. (a) Observed methine carbon region of the ^{13}C NMR spectrum recorded at 90.52 MHz in *n*-heptane at 67 °C. (b) Line spectrum of the methine carbons calculated at 67 °C to the pentad level. Line heights indicating relative intensities were obtained by integration of the methyl heptad resonances of the spectrum in Figure 1a. (c) Same as (b) except line heights were obtained assuming Bernoullian chain propagation statistics applied with a $P_m = 0.65$ obtained from the intensity of the methine (*mmmm*) pentad.

We tested the suitability of first-order Markovian statistics to our sample of atactic polypropylene by comparing the observed and expected relations[23] among tetrad, triad, and dyad intensities, e.g., $(mmr) = (mm)(mr)/(m)$. Significant deviations occurred between the expected and observed relations for at least three of the six tetrads. Apparently our polypropylene cannot be described by first-order Markovian statistics either.[17,18,26] It is our impression that no simple statistical model of polymerization is applicable to our sample of atactic polypropylene.

The agreement achieved between observed chemical shifts and those calculated from the short-range γ effect (interaction of carbons separated by three bonds) makes it clear that the observed long-range effects of stereosequence on the ^{13}C NMR chemical shifts of polypropylene are not due to comparable long-range interactions but instead result from the stereosequence dependent modification of local bond conformations. The RIS model of Suter and Flory[16] apparently gives a faithful accounting of the stereosequence dependent conformational characteristics of polypropylene as witnessed by the close correspondence between observed and calculated ^{13}C NMR chemical shifts.

We feel that our ability to assign, for the first time, virtually all of the resonances in each of the three regions of the ^{13}C NMR spectra of atactic polypropylene demonstrates the utility of predicting ^{13}C chemical shifts in vinyl

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polymers via the γ effect method. Such detailed assignment of resonances permits an accurate assessment of vinyl polymer microstructure and polymerization statistics and should aid in our search to understand their structure-dependent physical properties.

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(20) Freeman and Hill[19] have shown that in a repetitive sequence of $\pi/2$ pulses, a steady state is established in which an equilibrium exists between the effects of the radiofrequency pulses and spin relaxation. Assuming the pulse delay is $\geq 0.02T_1$, the longitudinal magnetization after three pulse periods can be determined by the expression $M^t_z = M_0(1 - e^{-t/T_1})[1 + ke^{-t/T_1} + (ke^{-t/T_1})^2]$, where M_0 is the equilibrium magnetization, t is the pulse interval or delay, T_1 is the spin–lattice relaxation time of the carbon observed, and k is a parameter reflecting deviations from a perfect $\pi/2$ pulse and normally is ≤ 0.1. For example, if one pulsed with a delay time t, equal to $1T_1$ of carbon A and $2T_1$ of carbon B, the resultant intensity observed for carbon A would be 66.0% of that observed with a delay of $5T_{1(A)}$, and the intensity observed for carbon B would be 88.2% of that obtained with a delay of $5T_{1(B)}$. Carbons A and B can be related quantitatively by multiplying the measured intensity of carbon A by a factor of 1.51 and the measured intensity of carbon B by a factor of 1.13. If we assume T_1 measurements with an accuracy of ±10%, our maximum experimental error in comparing carbon A and carbon B in this example would be to overestimate the amount of one carbon by 5% and underestimate the other carbon by 5%. Considering the long experimental times required in order to pulse at $5T_{1(\max)}$ intervals, the time saved by pulsing at $(1-3)T_1$ justifies the small error that may be introduced into the quantitative results.

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(22) In addition to the spectra presented in Figure 2, we have also recorded spectra in $CHCl_3$, C_6H_6, and 1,2,4-trichlorobenzene at T = 50–80 °C which further strengthen the observation that the patterns of methylene, methine, and methyl carbon chemical shifts are solvent independent.

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Copper(II) Ion Binding in Poly(glutamic acid)

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ABSTRACT: The complexation of the Cu(II) ion by poly(1-glutamic acid) (PGA) has been studied potentiometrically as a function of its initial degree of dissociation. Two different species, one with Cu bound to the carboxylate group in the repeating functional unit and the other with Cu bound to two repeating functional units through attachment to two carboxylate groups and the nitrogen of the chromophoric peptide group in one or both units, have been observed. The formation constant of CuA^+, the first species, is 4.0×10^1 in 0.05 M Na_2SO_4. A unique formation constant has not been established for the second species, CuA_2; with the first addition of Cu^{2+}, the formation constant, β_2^S, of the second species is approximately 2×10^4. The Cu appears to be bound more effectively with addition of more Cu until a second constant formation quotient that is unaffected by further addition of Cu is resolved. This second quotient, β_2^S, is larger when the PGA is initially more highly dissociated ($\beta_2^S \approx 7 \times 10^5$ at $\alpha > 0.45$, $\beta_2^S \approx 3.6 \times 10^5$ at $\alpha = 0.35$, and $\beta_2^S \approx 2 \times 10^5$ at $\alpha = 0.18$ and 0.25). The variability of β_2^S has been ascribed to (1) the contraction of the molecule with the addition of Cu(II) from a dimensionally stable expanded molecule to a dimensionally stable contracted molecule and (2) to a change in the accessibility of the repeating functional units for simultaneous interaction of carboxylate and peptide (A^{*-}) with Cu. Restraint of the accessibility of (A^{*-}) has been assumed to be smaller the larger the initial dissociation of the macromolecule.

The complexities that are encountered in the quantitative examination of metal–ion binding in weakly acidic (basic) polyelectrolyte systems have been fully discussed.[1-4] Their source is (1) the high and variable electric field at the surface of the polymers and (2), when more than one functional unit is bound to the metal ion, the inability to express the concentration of polymer species, charged and

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