where X_{12} is the exchange interaction parameter for the enthalpy, exclusively, and Q_{12} is the corresponding parameter for the exchange entropy. A is defined as

$$A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (X_{12}/P_1^*)(s_2/s_1) \quad (13)$$

The reduced residual partial molar enthalpy $\chi_{H,1}$ is

$$\chi_{H,1} = (c_1/\tilde{V}_1\tilde{T}_1)(1 + \alpha_1 T)(X_{12}/P_1^*[s_1/s_2]^2 - \tfrac{2}{3}[A\alpha_1 T]^2) \quad (14)$$

In these expressions X_{12} should be determined from the heat of mixing, but in this work X_{12} was determined from the relation of $\chi_{H,1} = -T(\partial\chi_1/\partial T)$. Since eq 4–7 are valid near the Θ temperature, $\chi_{H,1}$ was calculated from χ_1 determined from the intrinsic viscosity at 30 °C and atmospheric pressure. X_{12} is found to be 95.7 kg/cm^2. Q_{12} was determined by use of this X_{12} and the experimental χ_1 at 30 °C and atmospheric pressure to be -0.688 kg/cm^2 deg. These values are comparable with the values which Flory and Shih obtained, 81.6 kg/cm^2 and -0.398 kg/cm^2 deg for PDMS–cyclohexane and 112 kg/cm^2 and -0.653 kg/cm^2 deg for PDMS–chlorobenzene. A large negative value of Q_{12} is characteristic of PDMS solutions. Calculated pressure and temperature dependence of χ_1 at the Θ temperature and atmospheric pressure using the above values of X_{12} and Q_{12} and eq 12 are 1.23×10^{-5} cm^2/kg and -5.69×10^{-4} deg^{-1}, respectively. The contribution of the equation-of-state term containing A^2 in eq 12 to these values is very small. The predicted value of $(\partial\chi_1/\partial T)_P$ is in agreement with the value determined from the intrinsic viscosity, but predicted $(\partial\chi_1/\partial P)_T$ is positive, as in the case of the Patterson theory. These give positive $d\Theta/dP$, 2.16 $\times 10^{-2}$ deg/kg cm^{-2}. These deficiencies of the theoretical predictions, as pointed out by Patterson,[23] are unexplained.

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Calculated and Measured ^{13}C NMR Chemical Shifts of the 2,4,6-Trichloroheptanes and Their Implications for the ^{13}C NMR Spectra of Poly(vinyl chloride)

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ABSTRACT: ^{13}C NMR chemical shifts are measured for each of the carbon atoms in the three stereoisomers of 2,4,6-trichloroheptane (TCH). Spectra are recorded from solutions employing a broad range of solvents, as well as the neat liquids, over the temperature range of 25–140 °C. The differences in chemical shifts observed between the carbon atoms of the three TCH isomers are virtually independent of solvent for the methine carbons, only slightly solvent dependent for the methyl carbons, and extremely sensitive to solvent for the methylene carbons. The ^{13}C chemical shifts observed for TCH can be predicted, with the exception of those of the solvent-sensitive methylene carbons, by quantitatively calculating the number of three-bond gauche or γ interactions between carbon atoms and between carbon and chlorine atoms. The following γ effects are required to achieve this agreement: $\gamma_{CH_2 \text{ or } CH_3,CH} = -2.5$ ppm, $\gamma_{CH,CH_2 \text{ or } CH_3} = -5.0$ ppm, and $\gamma_{CH,Cl} = -3.0$ ppm, where $\gamma_{a,b}$ is the upfield shift observed at carbon a due to atom b, which is γ to a and in the gauche conformation. In addition to the ^{13}C chemical shifts of TCH and their temperature dependence, these γ effects correctly predict the chemical shift differences observed for the methyl and methine carbons between the meso and racemic isomers of 2,4-dichloropentane and the chemical shift pattern of the methine region in the ^{13}C NMR spectra of poly(vinyl chloride).

The most detailed information concerning the stereoconfiguration and/or sequence distribution of monomer units constituting vinyl homo- and copolymers is provided by ^{13}C NMR spectroscopy.[1-3] Recently one of the present

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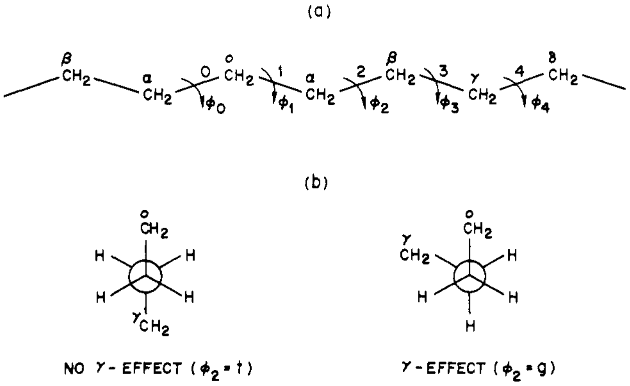


Figure 1. (a) Portion of a paraffinic hydrocarbon chain in the all trans, planar zigzag conformation; (b) Newman projections along bond two in (a) illustrating the γ effect.

authors demonstrated[4,5] that the observed stereochemical shifts in the ^{13}C resonance peaks can be attributed to conformational differences among the various stereosequences. On this basis, the ^{13}C chemical shift pattern observed in polypropylene[4] and ethylene–propylene copolymers[5] can be understood.

^{13}C NMR studies[6-9] of paraffinic hydrocarbons have made apparent 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 conformation (see Figure 1). The γ effect experienced by a given carbon atom in a vinyl polymer chain should therefore 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 rotation probabilities in vinyl polymers are known[10,11] to be sensitive to the stereosequence of the chain in the vicinity of the bond in question. Thus the suggestion[9,12] that the ^{13}C chemical shift pattern observed for a vinyl polymer is directly related to its conformational characteristics, as determined by the stereosequence of the chain, seems reasonable.

Bovey and Tonelli[9,13] were able to approximate the triad structure in the ^{13}C NMR methyl spectrum of atactic polypropylene (PP) by estimating the number of methyl carbon gauche interactions present in each triad and assigning each a γ effect of -4.3 ppm. The ^{13}C chemical shifts observed[14-16] for the 9-methyl carbon in the various stereoisomers of the PP model compound, 3,5,7,9,11,13,15-heptamethylheptadecane, including their temperature dependence, can be reproduced[4] by accounting for all possible γ interactions with a γ effect of -5.3 ppm.

The ^{13}C chemical shifts of the methylene carbon atoms in the isolated ethylene units ($-CH_2CH_2CH_2-$) of ethylene–propylene copolymers are also understandable[5] in terms of the γ effect, with $\gamma = -5.3$ ppm. Proposed effects of geometrical isomers and the stereo directing influence of the polymerization catalysts on the methylene ^{13}C chemical shifts[17-19] are easily evaluated and rationalized by comparison to the calculated chemical shifts.

On the other hand, a preliminary analysis[9,13] of poly(vinyl chloride) (PVC) with $\gamma_{C,C} = -4.3$ ppm and $\gamma_{C,Cl} = 0.0$ ppm did not lead to a satisfactory understanding of its ^{13}C NMR spectra. Consequently, we present here the results of our study of the ^{13}C chemical shifts, both measured and calculated, for the carbon atoms in the PVC model compounds, 2,4,6-trichloroheptanes (TCH).

Experimental Section

Synthesis and Separation of the Stereoisomers of 2,4,6-Trichloroheptane. 2,4,6-Trichloroheptane (TCH) has been prepared previously by reaction of heptane-2,4,6-triol with thionyl chloride.[20] The triol has been obtained from the corresponding trione by catalytic hydrogenation over Raney nickel[20a,b,21] or reduction with sodium borohydride.[22] Individual stereoisomers of TCH are secured most conveniently by gas chromatographic separation of their mixture,[23] although they can also be obtained by reaction of thionyl chloride with the separated stereoisomers of the triol.[20b] Yields of TCH realized in these earlier studies were either unspecified[20b,c] or very low,[20a] and although in one instance the catalytic hydrogenation step was reported to proceed in a yield of 80%[21] (vs. a triol yield of ca. 12% using sodium borohydride[22]), this method of reduction suffers from the necessity of using a pyrophoric catalyst under rather vigorous reaction conditions (e.g.,[21] ~2100 psi and 100–108 °C). In the present work, heptane-2,4,6-triol was obtained by catalytic hydrogenation of heptane-2,4,6-trione[24] under much milder conditions over a nonpyrophoric ruthenium catalyst. The triol was then converted into TCH by treatment with the complex formed from thionyl chloride and *N,N*-dimethylformamide.[25] Since development studies on these reactions are still in progress, publication of experimental details is being deferred to a later date.[26] However, it is already clear that this sequence comprises a greatly improved method for the synthesis of TCH. The TCH thus prepared contains the heterotactic (H), syndiotactic (S), and isotactic (I) stereoisomers in a ratio of ca. 2:1:1, respectively. In our work, these isomers were separated by gas chromatography on a Varian Aerograph instrument, Model 90-P, according to the procedure outlined by Flory and Pickles.[23c] The isomeric purities of the separated fractions were greater than 90%.

Other Materials. The poly(vinyl chloride) employed is a commercial material (No. 7649) obtained from Monomer-Polymer Laboratories. Integration of the spectrum in Figure 4 shows the P_m of the polymer equals 0.45.

Methods. The TCH solutions were prepared at concentrations of 0.5–2% v/v in 12-mm microcells. The microcell volume was 0.75 cm^3. Solutions were prepared using the following solvents: Me_2SO-d_6, acetone-d_6, and an 80/20 mixture of 1,2,4-trichlorobenzene/C_6D_6. In order to obtain the ^{13}C shifts of the neat material, the mixture of isomers was placed in a 5 mm capillary tube centered in a 12-mm tube. The volume between the 5 and 12 mm tubes was filled with $CDCl_3$ as an external lock. All measurements were made relative to internal Me_4Si or internal HMDS.

Measurements were made on a Varian XL-100 spectrometer with a ^{13}C resonance frequency of 25.16 MHz. Temperatures were measured with a calibrated thermocouple and a thermometer placed in a tube containing ethylene glycol. For all measurements of TCH the FID was stored in 8K computer locations; the $\pi/2$ sampling pulse was 15 μs; the pulse repetition time was 15.0 s; and all protons were noise decoupled. Depending on sample concentration, between 200 and 4000 scans were required for each measurement. The sweep width selected varied between 2000 and 4000 Hz depending on the solvent.

The data in Tables I and III were obtained by observing the mixture of isomers in solution. In order to assign the resonances of the mixture, it was necessary to measure the ^{13}C NMR shifts of each separated isomer in each solvent. In the measurements conducted at various temperatures, each separated isomer was again examined at each temperature in order to confirm the assignments of the mixture at that temperature.

The poly(vinyl chloride) was observed as a 20% w/v solution in 1,2,4-trichlorobenzene (TCB). In order to obtain the ^{13}C spectrum of PVC in TCB it was necessary to lock on external ethylene-d_4 glycol. Chemical shift measurements were made relative to internal HMDS. The spectrum of PVC in TCB was obtained on a Bruker HX-360 spectrometer at a carbon frequency of 90.52 MHz, using a sweep width of 12000 Hz in 32K data locations at a repetition rate of 2.0 s and a $\pi/2$ pulse of 25 μs.

Calculations

The three state (t, g, $\bar{g}$) rotational isomeric state (RIS) model of PVC developed by Williams, Flory, and Pickles[23c,27] which was based on epimerization studies of the 2,4-dichloropentanes (DCP) and TCH was used to

Table I
^{13}C Chemical Shifts (vs. Me_4Si) for the Carbon Atoms in the Stereoisomers of TCH at 33 °C

carbon atom	acetone	stereoisomer	TCB/C_6D_6	stereoisomer	Me_2SO	stereoisomer	neat
methine	59.46	S_C[a]	58.07	S_C	59.17	S_C	58.42
	58.49	H_C	57.20	H_C	58.13	H_C	57.49
	57.64	I_C	56.20	I_C	57.35	I_C	56.58
	56.47	S_E	54.98	H_E	56.40	S_E	55.39
	56.47	H_E	54.87	S_E	56.30	H_E	55.33
	55.31	I_E	53.95	I_E	55.23	I_E	54.28
	55.31	H_E	53.72	H_E	55.23	H_E	54.19
methylene	49.22	H	48.81	S	47.88	H	48.89
	49.02	S	48.58	H	47.51	I	48.78
	48.52	I	48.14	H	47.37	S	48.11
	48.13	H	47.49	I	46.64	H	47.87
methyl	25.69	S	25.34	H	25.31	H	25.78
	25.69	H	25.34	S	25.31	S	25.78
	24.76	H	24.10	I	24.47	H	24.67
	24.49	I	24.02	H	24.12	I	24.55

[a] E, C denote end and center methine carbons (see Figure 2).

Table II
Calculated Chemical Shift Differences (Δν, ppm) for the Carbon Atoms in the Stereoisomers of TCH

		Δν, ppm					
carbon atoms	stereoisomers	0 °C	25 °C	50 °C	75 °C	100 °C	150 °C
methine (E)[a]	I	−0.656	−0.682	−0.708	−0.739	−0.770	−0.882
(C)	I	−5.434	−5.426	−5.412	−5.412	−5.416	−5.446
(E)	S	−0.186	−0.259	−0.334	−0.412	−0.491	−0.654
(C)	S	−3.152	−3.232	−3.312	−3.402	−3.486	−3.674
(E)	H[b]	−0.901	−0.904	−0.910	−0.918	−0.918	−0.964
(C)	H	−4.032	−4.076	−4.129	−4.192	−4.259	−4.422
(E)	H	0	−0.030	−0.062	−0.094	−0.140	−0.234
methylene	I	−0.768	−0.778	−0.788	−0.800	−0.813	−0.843
	S	−0.053	−0.093	−0.133	−0.175	−0.220	−0.315
	H[b]	−1.085	−1.070	−1.055	−1.043	−1.033	−1.018
	H	0	−0.030	−0.063	−0.098	−0.138	−0.225
methyl	I	−1.415	−1.388	−1.360	−1.338	−1.318	−1.288
	S	−0.038	−0.080	−0.123	−0.168	−0.213	−0.308
	H[b]	−1.130	−1.130	−1.133	−1.135	−1.140	−1.153
	H	0	−0.033	−0.070	−0.113	−0.158	−0.263

[a] E, C denote end and center methine carbons (see Figure 2). [b] Carbon atoms in the racemic portion of the heterotactic 2,4,6-TCH isomer.

calculate the bond rotation probabilities for each of the nonterminal bonds in TCH (see Figure 2) at T = 0, 25, 50, 75, 100, 150 °C. Matrix multiplication methods[28] were utilized in these calculations.

From the bond rotation probabilities (see Table IV), the numbers of three bond gauche arrangements, or γ interactions, between pairs of carbon atoms and between carbon and chlorine atoms were obtained. The numbers of γ interactions were determined for all carbon atoms in each of the three isomers of TCH, i.e., isotactic (I), syndiotactic (S), and heterotactic (H). Multiplication of the number of γ interactions involving a given carbon atom by the appropriate γ effect leads to the predicted upfield ^{13}C chemical shift of that carbon atom.

Results

The results of the ^{13}C NMR measurements (e.g., see Figure 2) are presented in the form of line spectra in Figure 3 to facilitate comparison with the calculated chemical shifts. Experimental chemical shifts are presented in detail in Table I.

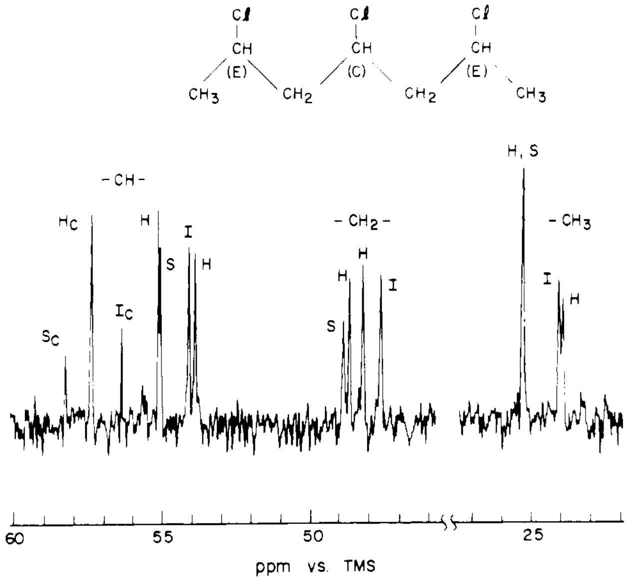


Figure 2. ^{13}C NMR spectrum of the mixed TCH isomers dissolved in TCB/C_6D_6 at 33 °C.

Calculated ^{13}C NMR chemical shifts based on the γ effect are presented in Table II. All of the entries in Table II result from $\gamma_{CH,CH_2\text{ or }CH_3} = -5.0$ ppm, $\gamma_{CH_2\text{ or }CH_3,CH} = -2.5$ ppm, and $\gamma_{CH,Cl} = -3.0$ ppm, where $\gamma_{a,b}$ is the upfield chemical shift observed at carbon a due to the presence of the γ substituent, atom b in a gauche arrangement with a. These values of γ produce the calculated line spectrum at the bottom of Figure 3. Table III contains the calculated and experimental temperature dependence of the chemical shifts.

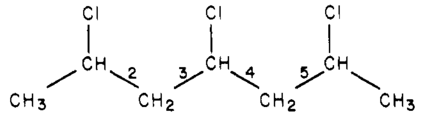
Comparison of Results and Discussion. The most striking feature of the experimental ^{13}C NMR spectra of the TCH isomers is the marked solvent sensitivity of the

Table III
Calculated and Observed Temperature Dependence of the ^{13}C Chemical Shifts for the Carbon Atoms in the Stereoisomers of TCH

carbon atom	stereo-isomer	$\Delta\nu$,[a] ppm (for ΔT = 140-25 °C) exptl (Me$_2$SO)	$\Delta\nu$,[a] ppm (for ΔT = 140-25 °C) calcd
methine (E)	I	−0.09	−0.13
(C)	I	−0.09	0.02
(E)	S	−0.35[b]	−0.35
(C)	S	−0.28	−0.38
(E)	H	−0.13	−0.02
(C)	H	−0.13	−0.26
(E)	H	−0.25	−0.22
methylene	I	−0.19	−0.05
	S	−0.58	−0.19
	H	0.06[b]	0.06
	H	−0.54	−0.16
methyl	I	0.11[b]	0.11
	S	−0.22	−0.20
	H	−0.09	−0.01
	H	−0.18	−0.18

[a] Negative $\Delta\nu$ indicates an upfield chemical shift with increasing temperature. [b] Observed chemical shift difference forced to agree with calculated value. This correction, attributable to the temperature dependence of the solvent sensitivity, was applied to the remaining observed chemical shift differences for like carbon atoms.

Table IV
Calculated Rotation Probabilities for the Bonds in TCH



bond	$P_{t,g,\bar{g}}$ I	$P_{t,g,\bar{g}}$ S	$P_{t,g,\bar{g}}$ H
2	0.408,[a] 0.436[b]	0.931,[a] 0.878[b]	0.511,[a] 0.507[b]
	0.571, 0.526	0.065, 0.111	0.471, 0.457
	0.021, 0.038	0.004, 0.011	0.018, 0.036
3	0.658, 0.644	0.932, 0.881	0.541, 0.556
	0.320, 0.314	0.063, 0.107	0.441, 0.407
	0.022, 0.042	0.005, 0.012	0.018, 0.037
4	0.658, 0.644	0.932, 0.881	0.957, 0.914
	0.320, 0.314	0.063, 0.107	0.039, 0.074
	0.022, 0.042	0.005, 0.012	0.004, 0.012
5	0.458, 0.436	0.931, 0.878	0.950, 0.900
	0.521, 0.526	0.065, 0.111	0.046, 0.089
	0.021, 0.038	0.004, 0.011	0.004, 0.011

[a] T = 25 °C. [b] T = 100 °C.

methylene carbon chemical shifts (Figure 3, Table I). By contrast the methine and methyl carbon chemical shifts show almost no and very little dependence on solvent, respectively.[29]

It is therefore not surprising that the chemical shifts calculated for the methylene carbons which take no account of the solvent depart significantly from the observed shifts in most solvents (see Figure 3). The solvent-independent methine regions of the TCH spectra are well reproduced by the chemical shifts calculated[30] for the methine carbons in each of the TCH isomers. The observed temperature dependence of the methine chemical shifts is also satisfactorily reproduced (see Table III) by the calculated shifts (Table II) based on the γ effect and evaluated from the RIS model of PVC.

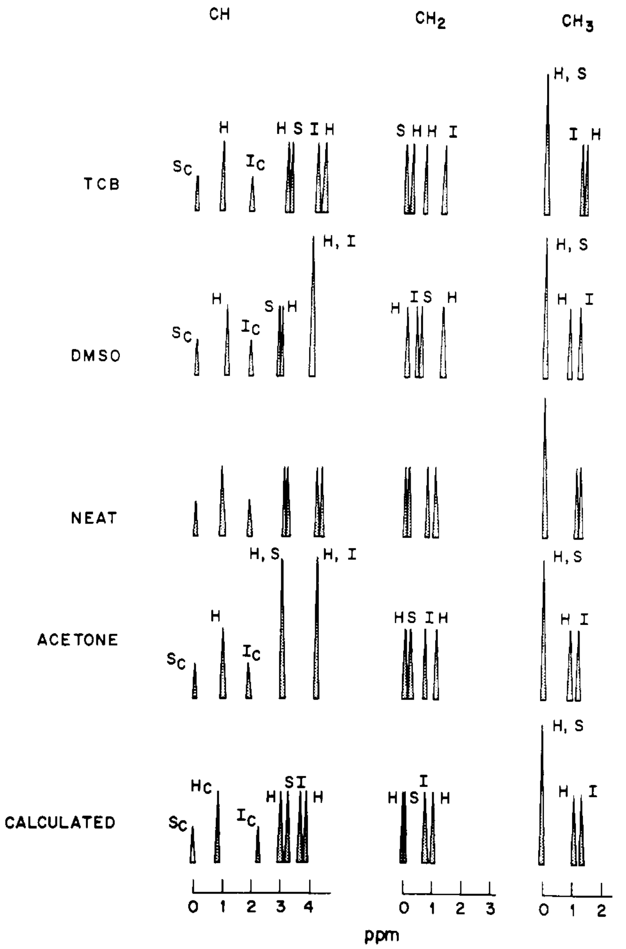


Figure 3. Comparison of measured (33 °C) and calculated ^{13}C chemical shifts of the TCH isomers in several solvents. The most downfield resonance in each of the three spectral regions is assigned a 0.0 ppm chemical shift.

Although the methyl regions of the TCH spectra exhibit some solvent sensitivity, the chemical shifts calculated for the methyl carbons in each TCH isomer generally approximate the observed ^{13}C NMR pattern including the total breadth of the methyl region. This agreement lends support to the assignment of $\gamma_{CH_2 \text{ or } CH_3,CH} = -2.5$ ppm to describe the γ effect produced by a tertiary carbon with a chlorine atom attached.

The chemical shift differences between methyl and methine carbons in the meso and racemic DCP's observed by Ando et al.[31] in a variety of solvents can also be rationalized with $\gamma_{CH,CH_2 \text{ or } CH_3} = -5.0$ ppm, $\gamma_{CH_2 \text{ or } CH_3,CH} = -2.5$ ppm, and $\gamma_{CH,Cl} = -3.0$ ppm. These γ effects lead to the prediction that both the methine and methyl carbons in *meso*-DCP will resonate ca. 1 ppm upfield from the same carbons in *racemic*-DCP. Ando et al.[31] find just such an upfield shift in the methyl and methine resonances of *meso*-DCP.

The temperature dependencies of the methylene and methyl carbon resonances observed in TCH are also satisfactorily reproduced by the calculated chemical shifts (see Table III).

A further test of the γ effects derived from our study of TCH ^{13}C NMR spectra is provided by comparing the chemical shifts of the central (C) methine carbons in I,S,H-TCH (see Table I) with the chemical shift of C$_4$ in heptane.[7] After correcting for the 31.2 ppm downfield shift expected[32] at each of the central methine carbons in TCH due to the α-chlorine substituent, the differences in chemical shift observed for the central methines in TCH and for C$_4$ in heptane are expected to be related to the differences in γ interactions involving each of these carbon atoms.

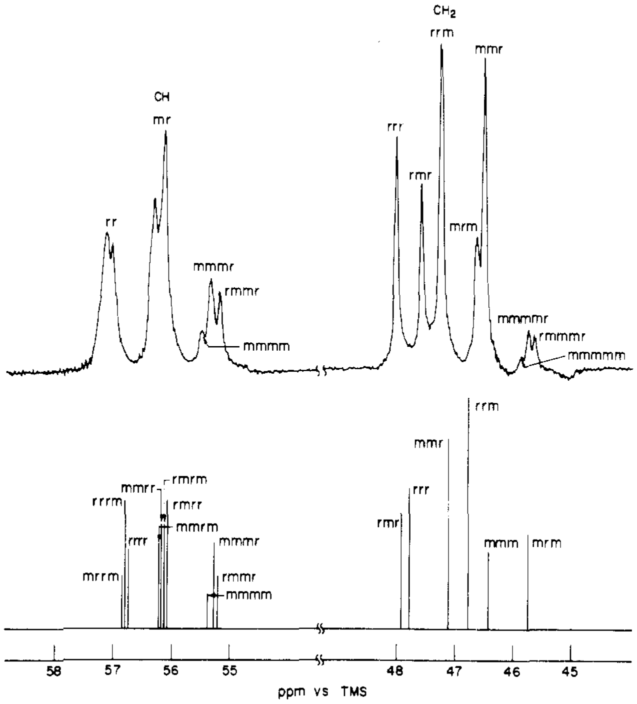


Figure 4. Comparison of measured ^{13}C NMR spectrum of atactic PVC ($P_m = 0.45$) dissolved in TCB at 120 °C with the chemical shifts calculated from evaluation of γ effects.

Bond rotation probabilities calculated previously[33-35] for heptane were used to evaluate the number of γ interactions involving C_4. Comparison of the observed chemical shifts for the central methine carbons in I,S,H-TCH with the chemical shift of C_4 in heptane[7] and accounting for the differences in the number of γ interactions led to the following values for the γ effects involved: $\gamma_{CH,CH_2 \text{ or } CH_3} = -4.9$ ppm and $\gamma_{CH,Cl} = -2.8$ ppm. Both γ effects are close to the -5.0 and -3.0 ppm values derived from the ^{13}C NMR data of the TCH isomers.

In Figure 4 the ^{13}C NMR spectrum of an atactic PVC dissolved in TCB at 120 °C is presented along with the calculated ^{13}C chemical shifts of the methine carbons in all possible pentad stereosequences and the methylene carbons in all possible tetrad stereosequences. Based on the results of our TCH studies, we adopted $\gamma_{CH_2,CH} = -2.5$ ppm, $\gamma_{CH,CH_2} = -5.0$ ppm, and $\gamma_{CH,Cl} = -3.0$ ppm and determined the number of γ interactions involving the central methine carbon in each pentad at 120 °C. The assignments marked on the experimental peaks were made independently based on the polymerization statistics[12] which lead to the overall atactic nature ($P_m = 0.45$) of this PVC sample. Clearly the correspondence between calculated and observed chemical shifts in the methine region of this PVC sample is close, and it confirms the γ-effect model of the ^{13}C chemical shifts in PVC derived from our study of the TCH isomers.

On the other hand, the methylene portion of the spectrum obtained in 100% TCB differs markedly from the predicted ^{13}C chemical shifts. The solvent dependence of the methylene carbon region in ^{13}C NMR spectra of PVC, which has been noted previously,[36] is not unexpected based on the results of our studies of the TCH's and Ando et al.'s[31] study of DCP's in a variety of solvents.

What types of solvent–polymer interactions can produce an extreme sensitivity to solvent for the ^{13}C chemical shifts of the methylene carbons, including a marked temperature dependence of the solvent effect, while the methine carbon resonances are virtually independent of the solvent medium? They are clearly not solvent-induced conformational changes, because in TCH and PVC the same bond rotations are involved in the γ effects of both the methylene and methine carbons, and yet only the methylene carbons exhibit solvent-dependent ^{13}C chemical shifts. In fact, in DCP the methylene carbon has no opportunity to participate in conformation-dependent γ interactions, yet its chemical shift also shows[31] a solvent sensitivity.

Clearly solvent–polymer interactions which produce this selective sensitivity must be local in nature and quite specific. We hope to learn more about these interactions through careful studies of the ^{13}C NMR spectra of TCH and PVC in a wide variety of solvents including ^{13}C NMR relaxation measurements. Chain dynamics obtained from the relaxation studies may help to detail the nature of the solvent–polymer interactions which are so vividly illustrated in the methylene portions of the ^{13}C NMR spectra.

Appendix.

Calculated rotation probabilities for the bonds in TCH are given in Table IV.

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(29) The chemical shift differences between the methine carbon resonances in the three stereoisomers of TCH are virtually independent of solvent, while those of the methyl carbons are only slightly solvent sensitive. Only the chemical shift differences, and not the absolute values, are insensitive to solvent.

(30) In constructing the line spectrum in Figure 3 corresponding to the calculated ^{13}C chemical shifts, each of the central (C) methine (see Figure 2) carbon resonances had to be shifted downfield by ca. 6.0 ppm, because the C-methine carbon has one additional β-carbon substituent compared to the end (E) methine carbons. This value for the β effect[6–9] was arrived at by comparing the chemical shift difference observed between the C and E methine carbons in each of the TCH isomers and assigning this difference, after correction for the different number of γ effects involving C and E methine carbons, to the β effect between neighboring methine carbons. The value arrived at (6.2 ± 0.5 ppm) is similar to the β effect caused by other tertiary carbon atoms reported in the literature.[6–9] In addition the consistent set of β effects obtained for the TCH isomers also supports $\gamma_{\mathrm{CH,CH_2\ or\ CH_3}} = -5.0$ ppm and $\gamma_{\mathrm{CH,Cl}} = -3.0$ ppm.

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Carbon-13 Chemical Shifts of the Polypropylene "Model" Compounds 3,5-Dimethylheptane and 3,5,7-Trimethylnonane

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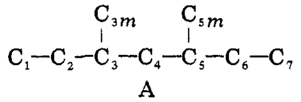
ABSTRACT: ^{13}C-NMR chemical shifts are calculated for the stereoisomers of the polypropylene model compounds 3,5-dimethylheptane (A) and 3,5,7-trimethylnonane (B). Differences in the chemical shifts of the same carbon atom in the various stereoisomers are attributed to stereosequence-dependent differences in the frequency with which the given carbon atom is involved in 3 bond gauche or γ interactions with other carbon atoms. The Suter–Flory RIS model of polypropylene is employed in the evaluation of the number of γ interactions involving each of the carbon atoms in A and B. The calculated ^{13}C chemical shifts are compared to the observed values and those calculated previously for 3,5,7,9,11,13,15-heptamethylheptadecane. This comparison permits an assessment of the utility of A and B as model compounds for polypropylene.

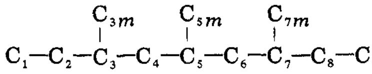
It was recently demonstrated[1,2] that the ^{13}C-NMR spectra of polypropylene can be understood based on the stereosequence sensitive γ effect.[3–6] ^{13}C chemical shifts expected at the 9-C$^{\alpha}$ and CH$_3$ carbons and at the 8 and 10-CH$_2$ carbons in the various stereoisomers of the polypropylene model compound 3,5,7,9,11,13,15-heptamethylheptadecane (C) were evaluated[1] with a 3 bond gauche or γ interaction of −5.3 ppm by employing the rotational isomeric state (RIS) model of polypropylene derived by Suter and Flory.[7] Very good agreement was achieved between the calculated and observed[8–10] chemical shifts for the carbon atoms in C[1] and polypropylene.[2]

Ritter et al.[11] have reported a temperature-dependent study of the ^{13}C chemical shifts of the various stereoisomers of 3,5-dimethylheptane (A) and 3,5,7-trimethylnonane (B),



$$\begin{array}{ccccccccccccc} & & & & C_{3m} & & & & C_{5m} & & & & \\ & & & & | & & & & | & & & & \\ C_1 & - & C_2 & - & C_3 & - & C_4 & - & C_5 & - & C_6 & - & C_7 \end{array}$$

A



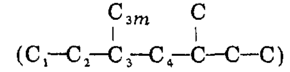
$$\begin{array}{ccccccccccccccccc} & & & & C_{3m} & & & & C_{5m} & & & & C_{7m} & & & & \\ & & & & | & & & & | & & & & | & & & & \\ C_1 & - & C_2 & - & C_3 & - & C_4 & - & C_5 & - & C_6 & - & C_7 & - & C_8 & - & C_9 \end{array}$$

B

which may also serve as model compounds of polypropylene. They observed throughout the temperature range 150–300 K, and even upon extrapolation to 0 K, that the chemical shift differences between the corresponding carbon atoms in the different stereoisomers do not coincide for compounds A and B. Only the chemical shift differences observed in B correspond to those measured for polypropylene, which seems to render A useless in the study of polypropylene.

It appears useful to apply the same procedures, used to successfully evaluate the ^{13}C chemical shifts of the much larger model compound C[1], to compounds A and B in an attempt to also understand their conformational and configurational characteristics. This is carried out in the present report, where the results obtained for A and B are

Table I
Calculated ^{13}C-NMR Chemical Shift Differences $\Delta\nu$ (ppm) for the Carbon Atoms in the Meso and Racemic Isomers of Model Compound A

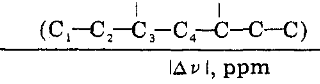


$$\begin{array}{ccccccccccccc} & & & & C_{3m} & & & & C & & & & \\ & & & & | & & & & | & & & & \\ (C_1 & - & C_2 & - & C_3 & - & C_4 & - & C & - & C & - & C) \end{array}$$

carbon atom	$\Delta\nu$,[a] ppm			
	150 K	200 K	250 K	300 K
1	−0.180	−0.170	−0.154	−0.145
2	1.023	1.055	1.012	0.943
3	−0.006	−0.021	−0.037	−0.063
3*m*	−0.724	−0.785	−0.779	−0.753
4	−0.302	−0.297	−0.265	−0.243

[a] Negative values of $\Delta\nu$ indicate that the resonance of the carbon atom in the racemic isomer will occur upfield from its resonance in the meso isomer.

Table II
Comparison of Experimental[5,11] and Calculated ^{13}C Chemical Shift Differences $\Delta\nu$ for the Carbon Atoms in the Meso and Racemic Isomers of Model Compound A



$$\begin{array}{ccccccccccccc} & & & & C_{3m} & & & & C & & & & \\ & & & & | & & & & | & & & & \\ (C_1 & - & C_2 & - & C_3 & - & C_4 & - & C & - & C & - & C) \end{array}$$

carbon atom	$\lvert\Delta\nu\rvert$, ppm			
	150 K		300 K	
	exptl[11]	calcd	exptl[11]	calcd
1		0.18	(0.2)[a]	0.15
2	2.0	1.02	1.15 (1.0)	0.94
3	0.50	0.01	0.14 (0.1)	0.06
3*m*	1.03	0.72	0.71 (0.7)	0.75
4	0.10	0.30	0.16 (0.2)	0.24

[a] Taken from ref 5 where ^{13}C-NMR spectra were recorded in a 50:50 v/v mixture of A-dioxane.

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