# Carbon-13 Nuclear Magnetic Resonance Relaxation Measurements in Methyl-Substituted Alkanes. Application to Molecular Dynamics and Chemical Shift Assignments

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ABSTRACT: Correlation times are determined from $^{13}C$ NMR spin–lattice relaxation measurements at 22.63 MHz and from kinematic viscosity measurements for 2,5,8,11-tetramethyldodecane (TMDO) and 2,6,10,14-tetramethylpentadecane (TMPD) at a single temperature and 2,8,14,20-tetramethylheneicosane (TMHE) as a function of temperature (310–359 K). Maximum NOE values are observed for all carbons. Activation energies determined from macroscopic viscosity measurements on TMHE are of comparable magnitude to those obtained from relaxation data. Molecular dynamics of terminal and interior methyl branches and branch points can be distinguished. The contribution of internal motion to overall reorientation increases from the interior of the molecule outward regardless of the number of methylenes separating branch points. TMHE is the largest branched-chain liquid hydrocarbon compound yet employed as a model for understanding propylene based polymer dynamics. The relative contribution of overall reorientation to the interior branch points is still greater than that in polymers. Several $^{13}C$ chemical shift assignments for these compounds have been changed to be consistent with their molecular dynamics. These major changes in the assignment of observed chemical shift nonequivalences are discussed together with implications for assignments in polypropylene and ethylene–propylene rubbers.

NMR relaxation times and Nuclear Overhauser enhancements have been greatly facilitated by the availability of modern Fourier transform instrumentation.[2,3] It is now well established that carbon-13 spin–lattice relaxation times ($T_1$) can be used to obtain information on the molecular dynamics of compounds in the liquid state.[4–10] The technique is also applicable to proteins in solution, lipid bilayers, and polymers.[11–22]

Since $T_1$ is a function of correlation times of motions causing relaxation, a quantitative description of molecular dynamics from $T_1$ data requires the explicit functional dependence of $T_1$ on one or more correlation times necessary to describe a given motional model. In general quantitative information on molecular dynamics can be obtained only for rigid spherical or axially symmetric ellipsoidal systems.[23] The introduction of internal motions (single or multiple) which enhance the flexibility of the system severely complicates the situation. In the case of single internal motions in molecules which reorient isotropically the treatment of Woessner applies.[24] The treatment of Wallach provides the basis for multiple internal rotations[25] and has been extended to include anisotropic overall reorientation.[26] Levine et al. developed a method based on the Wallach approach for multiple internal motions considering independent rotational diffusion about carbon–carbon bonds with which both isotropic as well as anisotropic overall motion could be treated.[27,28] These calculations ignored steric hindrance to motion and conformation correlations about adjacent bonds. Levine points out in a later paper that realistic models of alkane chain internal rotation must include both population ratios of gauche to trans conformations and the average lifetime in the trans conformation.[29] Since $^{13}C$ NMR may only yield a single relaxation time for each carbon, rigorous interpretation of $T_1$ values has been hampered because of the problem of fitting the models to this underdetermined system. A number of theoretical investigations in polymer segmental motion have been reported.[30–34]

The single correlation time model of segmental reorientation has provided the basis for a large quantity of work. Evidence, however, points out the shortcomings of this approach in certain cases. Schaefer used a distribution of correlation times to explain $T_1$, $T_2$, and NOE's for both bulk and dissolved polymers.[32] Herman and Weill have also elaborated on this point.[33] Cole–Cole distributions,[35,36] log $\chi^2$ distribution of correlation times,[37] and nonexponential correlation functions of Monnerie et al.[34,40] have been applied to explain $T_1$, $T_2$, and NOE data. The results of Heatley[39] indicate chain segmental motion loses correlation in two to three monomer units or six methylene units. He also showed that the three theoretical models, referred to above, equally fit the observed $T_1$ and NOE data. Jones et al. find a "five-bond" correlation in poly(*p*-fluorostyrene) and poly(*m*-fluorostyrene).[40]

The purpose of the present paper is to provide $T_1$ information for 2,8,14,20-tetramethylheneicosane (TMHE) over the temperature range from 310 to 359 K and 2,5,8,11-tetramethyldodecane (TMDO) and 2,6,10,14-tetramethylpentadecane (TMPD) at 310 K. The approach in this work is basically one of providing additional relaxation data on branched chain hydrocarbons from which the qualitative features of dynamics of chain motion can be obtained. A similar approach has recently[41] been used for understanding polymer motion from *n*-alkanes[42] as model compounds. Realistically, the complex multiple internal rotations of these branched chain systems make detailed treatment of motional models difficult. However, it is felt that the present work provides a basis for which a more complete description can be formulated. In addition these compounds exhibit both configurational and conformational structure and it was of interest to ascertain their influence upon the dynamic NMR behavior of this molecule.

## Experimental Section

Measurements were performed on a WH-90 pulse Fourier transform spectrometer operating at 22.63 MHz. The Bruker (B-ST 100/700) variable temperature apparatus was used to control the sample temperature. The thermocouples were calibrated by a Mettler FP-52 hot stage which contains a platinum resistance thermometer. The furnace of the hot stage is accurate to ±0.1 °C (calibrated by selected standards whose triple points are known to ±0.05 °C). The temperature of the sample cell was obtained by means of a calibration chart which measures the interior sample temperature as a function of the Bruker thermocouple temperature and nitrogen gas flow. The pulse power was such that the $^{13}C$ magnetization was rotated 90° in 8.0 $\mu$s.

Spectra were obtained using a spectral width of 1 kHz and 8K data points and were Fourier transformed (BNC-12 computer) to yield a resolution of 0.24 Hz.

Relaxation experiments were made with the standard inversion-recovery sequence (180–$\tau$–90) using a repetition time $\geqslant 5T_1$. One hundred free induction decays (FID) were accumulated for each value of $\tau$ in the relaxation experiment. Fifteen to twenty $\tau$ values were used and the data were fit to the standard exponential function using nonlinear regression techniques. The 95% nonlinear confidence intervals were obtained as standard output from the statistical section of the program. The parameters varied were the equilibrium magnetization and the $T_1$ value. The 180° pulse width was determined experimentally. The actual calculations were performed with the two adjustable parameters. We did not attempt to use the inverting pulse flip angle as a variable parameter since this parameter and the $T_1$ value are highly correlated. The $T_1$ values were determined from the time dependent peak heights.

The hydrocarbons were provided by Dr. E. C. Gregg, Jr., BFGoodrich Research and Development Center, Brecksville, Ohio. The samples for $T_1$ determination were prepared by vacuum degassing (freeze–thaw pump method) the liquid in Wilmad Cylindrical cells and sealing under vacuum. These cells were contained in a standard 10-mm NMR tube. Deuterium oxide was placed on the outside of the cell to provide internal lock. The cell arrangement insured that the sample was contained in the carbon-13 transmitter and receiver coil.

The NOE measurements at 310 K utilized a gated decoupling technique. The NOE values were obtained from the ratio of intensities of the fully decoupled to gated decoupled intensities (areas). In the gated mode the decoupler was gated on during data acquisition. The repetition rate was such that a waiting time of $\sim 10T_1$ (for slowest relaxing carbon) was obtained between sequential experiments. Verification of these results was provided by independent measurements carried out on these compounds using the gated decoupling technique with a Bruker SXP spectrometer equipped with a four-pulse programmer. Corroborating data were obtained at the BFGoodrich Research and Development Center.

Kinematic viscosities were determined using a Cannon-Ubbelohde (Fisher 318) viscometer previously calibrated with distilled water. The temperature was controlled to ±0.05 °C. Densities were measured by pycnometry.

## Results

Table I gives the $T_1$ values obtained for TMHE over the temperature range 310–359 K. The assignments are based on the results of Carman, Tarpley, and Goldstein.[43]

$^{13}$C Nuclear Overhauser enhancements (NOE) were determined for the resolved carbon lines at 310 K for all branched alkanes. The data indicate a maximum NOE at this temperature for all carbons (3.00 ± 0.2) from which it can be concluded that maximum NOE values are also obtained at the higher temperatures employed in TMHE. These results are consistent with a heteronuclear dipolar mechanism for $^{13}$C relaxation. Furthermore, the maximum NOE indicates that the rotational correlation times are such that the extreme narrowing condition is valid (i.e., $(\omega_H + \omega_C)^2\tau_c^2 \ll 1$ where $\omega_H$ and $\omega_C$ are the proton and carbon Larmor frequencies). The spin–lattice relaxation time for a $^{13}$C nucleus arising from dipole–dipole interactions with directly bonded protons is given by

$$\frac{1}{NT_1} = \frac{1}{10}\frac{\gamma_H{}^2\gamma_C{}^2\hbar^2}{r_{CH}{}^6}\chi(\tau_c) \tag{1}$$

where

$$\chi(\tau_c) = \frac{\tau_c}{1 + (\omega_H - \omega_C)^2\tau_c{}^2} + \frac{3\tau_3}{1 + \omega_C{}^2\tau_c{}^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2\tau_c{}^2} \tag{2}$$

here $\tau_c$ is a single correlation time expressing the exponential decay of the motional autocorrelation function; $\gamma_C$ and $\gamma_H$ are the gyromagnetic ratios for $^{13}$C and $^1$H, respectively; $r_{CH}$ is the C–H bond length (taken as 0.109 nm); and $N$ is the number of directly bonded protons. The NOE of the carbon signal upon irradiation of the protons is given by[10,42]

$$(\eta + 1) = \frac{1}{\chi(\tau_c)} \times \frac{\gamma_H}{\gamma_C}\left[\frac{6\tau_c}{1 + (\omega_H + \omega_C)^2\tau_c{}^2} - \frac{\tau_c}{1 + (\omega_H - \omega_C)^2\tau_c{}^2}\right] \tag{3}$$

in the "extreme narrowing limit" as mentioned above eq 1 and 3 reduce to

$$\frac{1}{NT_1} = \frac{\gamma_H{}^2\gamma_C{}^2\hbar^2}{r_{CH}{}^6}\tau_c \tag{4}$$

and

$$\mathrm{NOE} = (\eta + 1) = 1 + \gamma_H/2\gamma_C = 2.988 \tag{5}$$

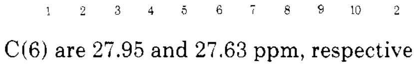
For the molecules studied here the tumbling times are on the order of picoseconds and eq 4 is obeyed. It should be pointed out that eq 4 considers only directly bonded protons. However, for the cases studied here the effects of more distant protons are negligible. For multiple correlation times $\tau_c$ must be replaced by "$\tau_{\mathrm{eff}}$" which is a weighted average of correlation times for individual motions that reorient a given C–H vector.[31,42]

Wallach[25] has suggested a procedure of calculating $\tau_{\mathrm{eff}} = \int_0^\infty G(t)\,dt$ where $G(t)$ is the autocorrelation function and substituting this in the expression for the reduced spectral density, $J(\omega_j) = \tau_i/(1 + \omega^2{}_j\tau_i{}^2)$, to yield an equation similar to eq 1 and 2. This procedure is correct under the following conditions:[27] (1) the autocorrelation function is a single exponential; and (2) if $\omega_j{}^2\tau_i{}^2 \ll 1$ for all $i$ and $j$ (i.e., the extreme narrowing condition must hold for all motions in the system). In the present system, condition 2 is fulfilled. $\tau_{\mathrm{eff}}$ values for TMHE are given in Table II as calculated from eq 4 by re-

### Table I
### $T_1$[a] Values for 2,8,14,20-Tetramethylheneicosane[b]

| $T$, K | C(3) | C(7,9) | C(8) | C(5,11) | | C(2) | C(4,[c]10) | C(6)[c] | C(1,2a) | C(12) |
|---|---|---|---|---|---|---|---|---|---|---|
| 310 | 0.84 | 0.33 | 0.51 | 0.48 | | 1.81 | 0.65 | 0.38 | 1.84 | 0.86 |
| 316 | 0.97 | 0.41 | 0.61 | 0.57 | | 2.06 | 0.79 | 0.47 | 1.96 | 0.94 |
| 322 | 1.29 | 0.50 | 0.74 | 0.70 | | 2.82 | 0.99 | 0.57 | 2.48 | 1.17 |
| 331 | 1.52 | 0.60 | 0.91 | 0.72 | 0.90 | 3.19 | 1.15 | 0.68 | 2.85 | 1.36 |
| 341 | 2.40 | 0.91 | 1.41 | 1.30 | | 4.93 | 1.81 | 1.03 | 3.89 | 1.86 |
| 352 | 2.42 | 0.93 | 1.43 | 1.11 | 1.38 | 4.95 | 1.78 | 1.05 | 3.99 | 1.91 |
| 359 | 3.71 | 1.43 | 2.22 | 1.97 | | 7.65 | 2.83 | 1.64 | 5.56 | 2.71 |

[a] In seconds. Errors ~5%. [b] Numbering scheme as follows:



$\mathrm{(C{-}\overset{C}{C}{-}C{-}C{-}C{-}C{-}C{-}\overset{C}{C}{-}C{-}\overset{C}{C}{-})C}$

[c] Correct chemical shift values for C(4) and C(6) are 27.95 and 27.63 ppm, respectively. See text.

**Table II**
**$\tau_{eff}$ Values[a] for 2,8,14,20-Tetramethylheneicosane**

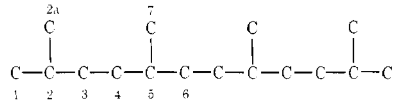
| $T$, K | C(3) | C(7,9) | C(8) | C(5,11) | | C(2) | C(4,10) | C(6) | C(1,2a) | C(12) |
|---|---|---|---|---|---|---|---|---|---|---|
| 310 | 28.0 | 71.4 | 92.4 | 49.1 | | 26.0 | 36.2 | 62.0 | 8.5 | 18.3 |
| 316 | 24.3 | 57.5 | 77.2 | 41.3 | | 22.9 | 29.8 | 50.1 | 8.0 | 16.7. |
| 322 | 18.3 | 47.1 | 63.7 | 33.7 | | 16.7 | 23.8 | 41.3 | 6.3 | 13.4 |
| | | | | 32.7 | 26.2 | | | | | |
| 331 | 15.5 | 39.3 | 51.2 | 29.2 | | 14.8 | 20.5 | 34.6 | 5.5 | 11.6 |
| 341 | 9.8 | 25.9 | 33.4 | 18.1 | | 9.6 | 13.0 | 22.9 | 4.0 | 8.4 |
| | | | | 21.2 | 17.1 | | | | | |
| 352 | 9.7 | 25.3 | 32.9 | 18.9 | | 9.5 | 13.2 | 22.4 | 3.9 | 8.2 |
| 359 | 6.4 | 16.5 | 21.2 | 12.0 | | 6.2 | 8.3 | 14.4 | 2.8 | 5.8 |

[a] In picoseconds. $\tau_{eff}$ equals $r_{CH}{}^6/KT_1N_H$ where $r_{CH}$ = 0.109 nm, $N_H$ is the number of attached protons, and $K$ equals 3.56 m/s$^2$.

**Table III**
**$T_1$ and $\tau_{eff}$ Values[a] for 2,5,8,11-Tetramethyldodecane[b] at 310 K**

| Carbon | $T_1$ | $\tau_{eff}$ |
|---|---|---|
| C(3 | 1.56 | 15.1 |
| C(4)[c] | 1.21 | 19.5 |
| | 1.20 | 19.6 |
| C(6)[c] | 1.01 | 23.3 |
| C(5) | 1.74 | 27.1 |
| C(2) | 3.30 | 14.3 |
| C(1,2a) | 2.16 | 7.3 |
| | 2.15 | 7.3 |
| C(7) | 1.63 | 9.6 |
| | 1.63 | 9.6 |

[a] Picoseconds. [b] Numbering scheme is as follows:

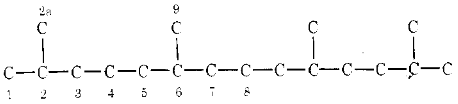


[c] Correct chemical shift value for C(6) is 35.29 ppm; the nonequivalent C(4) carbons are at 35.85 and 35.59 ppm. See text.

**Table IV**
**$T_1$ and $\tau_{eff}$[a] Values for 2,6,10,14-Tetramethylpentadecane[b] at 310 K**

| Carbon | $T_1$ | $\tau_{eff}$ |
|---|---|---|
| C(3) | 1.25 | 18.8 |
| C(7) | 0.60 | 39.2 |
| C(5) | 0.73 | 32.3 |
| C(6) | 1.02 | 46.2 |
| C(2) | 2.70 | 17.4 |
| C(4)[c] | 0.94 | 25.1 |
| C(8)[c] | 0.61 | 38.6 |
| C(1,2a) | 2.02 | 7.8 |
| | 2.02 | 7.8 |
| C(9) | 1.22 | 12.9 |

[a] Picoseconds. [b] Numbering scheme is as follows:



[c] Correct values for C(4) and C(8) are 25.28 and 24.95 ppm, respectively. See text.

**Table V**
**Activation Energies[a] for 2,8,14,20-Tetramethylheneicosane**

| Carbon position[b] | $\Delta E$, kJ/mol | Carbon position[b] | $\Delta E$, kJ/mol |
|---|---|---|---|
| C(3) | 26.8 ± 2.1 | C(6) | 25.5 ± 2.1 |
| C(7) | 25.5 ± 2.1 | C(4) | 25.5 ± 2.1 |
| C(8) | 26.0 ± 2.1 | C(1,2a) | 20.1 ± 1.7 |
| C(5,11) | 24.7 ± 2.1 | C(12) | 19.7 ± 1.7 |
| C(2) | 25.5 ± 2.1 | | |

[a] Preexponential factors ranged from 0.9 to 6.4 × $10^{-15}$ s.
[b] Numbering is as follows:

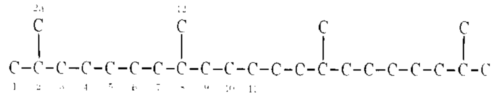


**Table VI**
**Kinematic Viscosities**

| | $T$, K | $\eta/\rho$, m$^2$ s$^{-1}$ × $10^6$ |
|---|---|---|
| 2,8,14,20-TMHE | 306 | 12.320 |
| | 310 | 10.820 |
| | 326 | 6.378 |
| | 346 | 3.897 |
| 2,5,8,11-TMDO | 310 | 2.523 |
| 2,6,10,14-TMPD | 310 | 4.199 |

placing $\tau_c$ with $\tau_{eff}$. For the purpose of this work we believe this procedure is satisfactory and the values obtained for TMHE are given in Table II.

$T_1$ and $\tau_{eff}$ data for TMDO and TMPD are given in Tables III and IV. Methyl substitution acts in a similar manner increasing $\tau_{eff}$ at the position of the substituent in relation to what would be expected from the corresponding $n$-alkane. The $\tau_{eff}$ are identical for methyl carbons 1 and 2a in TMDO, TMPD, and TMHE.

Carbons C(4) (C(6) before reassignment) and C(7) of TMDO show nonequivalent chemical shifts resulting from configurational differences. However, these structurally nonequivalent carbons have the same $\tau_{eff}$.

The thermal behavior of $\tau_{eff}$ for TMHE (over the temperature range studied) can be represented by an Arrhenius-type expression.

$$\tau_{eff} = \tau^0 e^{\Delta E/RT} \qquad (6)$$

(where $\tau^0$ is the preexponential factor and $\Delta E$ the activation energy). The range of activation energies for the methine and methylene carbons was 24.7–26.8 kJ/mol. However, the data for the isopropylmethyl and internal methyl carbons are 4.6 to 6.7 kJ/mol lower. The activation energies determined from least-squares fit of the data to eq 6 are found in Table V. The preexponential factor ranged from 0.9 to 6.4 × $10^{-15}$ s.

Densities and viscosities were determined for the three hydrocarbons studied at 310 K. In the case of TMHE measurements were made at three additional temperatures (see Table VI). Overall rotational rates were determined from the Gierer–Wirtz modification of the Stokes–Einstein equation. $\tau_0$ values for TMHE at the measured temperatures yield an activation energy of 28.5 ± 1.3 kJ/mol with a preexponential factor of $2.9 \times 10^{-15}$.

## Discussion

Previous observations on *n*-alkanes have led to the following general observations: (1) $\tau_{\mathrm{eff}}$ decreases from the center of the chain outward; (2) $\tau_{\mathrm{eff}}$ increases progressively for a given carbon as chain length increases; and (3) $\tau_{\mathrm{eff}}$ increases to a smaller extent at the chain ends as the length of the *n*-alkane increases.[28,42,44]

Two basic approaches have been adopted in interpreting the above observations in terms of the dynamics of detailed alkyl chain motions. In the more rigorous Levine approach[27] one calculates the correlation function of the combined motion of a defined molecular segment in the hydrocarbon chain (combined meaning overall isotropic or anisotropic motion of the molecule assumed rigid and internal motion). Internal motion is considered to be due to either stochastic rotational diffusion about individual C–C bonds or to jumps between three equally populated conformations (trans, gauche$^+$, gauche$^-$) of each bond. However, one should be aware that the model ignores steric hindrance to motion and conformation correlations about adjacent bonds. Consequently, application to branched chain systems is not straightforward since, among other things, the potential energy profile for each C–C bond changes along the chain.

Lyerla et al. suggested a simplified approach.[42] In this method C–H vector reorientation depends upon an overall isotropic rotation of the molecule (assumed rigid) with a rotational rate, $\tau_0^{-1} \equiv R_0$, and internal motion due to rotations about individual C–C bonds with rates $\tau_i^{-1} \equiv R_i$. The effective rate, $\tau_{\mathrm{eff}}^{-1} \equiv R_{\mathrm{eff}}$, is the sum of these:

$$R_{\mathrm{eff}} = R_0 + R_i \qquad (7)$$

In this model the internal rates are independent of the overall rotation rate. $\tau_0$ is a function of molecular weight, viscosity, and chain length dependent intermolecular interactions. The internal rates are due to conformational changes and if substituents, such as methyls, are present to internal rates within a given main-chain conformation.

In the discussion which follows we have chosen the simplified approach for several basic reasons. The Levine method is difficult to apply to branched chain hydrocarbons because it requires a knowledge of the potential energy profile about individual C–C bonds which is not readily available for the present branched chain alkanes. The simpler Lyerla method can be applied without this information and previous applications of this approach have led to reasonable conclusions.

To the extent that eq 7 is valid, it may be employed to separate the contributions from overall and internal motions. Estimates of $\tau_0$ can be found from the Gierer–Wirtz modification (with "microviscosity" correction) to the Stokes–Einstein formulation of rotational diffusion constants[46] (D)

$$\tau_0 = \frac{M_{\mathrm{w}}}{6.9 \times 10^6} (\eta/\rho)_T \qquad (8)$$

where $M_{\mathrm{w}}$ is the molecular weight and $\eta$ and $\rho$ are the absolute viscosity (P s) and density (kg/m$^3$). Since $\eta/\rho$ is the kinematic viscosity (m$^2$/s) measurement of the above quantity at the appropriate temperature is sufficient for an estimate of $\tau_0$.

The carbon skeletons of each molecule are presented in Table VII with the associated $R_i$ calculated from eq 7 and 8. Also given is the percent contribution of the internal rate to the total rate of motion ($[R_i/(R_i + R_0)] \times 100$). In addition, to TMDO, TMPD, and TMHE we have included several molecules, previously reported, pertinent to the present discussion.

The numbering scheme is identical to that of Carman, Tarpley, and Goldstein,[43] but several assignments have been changed as noted in the footnotes of Tables I, III, and IV, as explained below. Overall rates for TMDO, TMPD, and TMHE were obtained from the Gierer–Wirtz equation using measured kinematic viscosities. The $\tau_0$ values for the other three derivatives were estimated to be 72 ps from the kinematic viscosity for eicosane.

Several possible permutations of assignments are possible in the model compounds without creating severe disagreement with the substituent effect predictions based on the parameters of Grant and Paul.[47] In the case of TMDO one possible permutation involves C(6) at 35.29 ppm (previously[43] assigned as C(4)) with the nonequivalent C(4) at 35.85 and 35.59 ppm (previously assigned as C(6)). The present results indicate a contribution from internal motion to the overall rate of 13% at the old C(4) and 27% at the old C(6). Under the assumption that the internal contribution should increase on moving toward the end of the chain the previous assignments have been reversed.

Similarly, TMPD contains two carbons, C(8) at 24.95 ppm (previously C(4)) and C(4) at 25.28 ppm (previously C(8)). Both are $\beta$ to two methyl substituents with respective internal contributions of 27 and 52% to the overall rates. Here, reversing the previous assignments gives a smoothly increasing percent contribution to the internal rate from the center of the molecule outward. The reversal in Tables III and IV implied in the above statements becomes more convincing if one compares TMPD with 2,6,11,15-TMHD. In TMHD C(4) is $\beta$ to C(2) and C(6) while C(8) is $\beta$ to C(6) but $\gamma$ to the remaining interior point of substitution. In this case the percent contribution to the internal rate increases smoothly toward the chain end and there is no possibility of chemical shift assignment reversal.

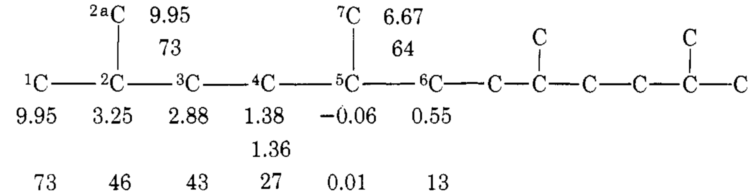
We have corrected a typographical error in Table I of ref 43 for TMHE assignments. The chemical shift of C(4) should be 27.95 ppm and for C(6) 27.63 ppm based on intensity measurements. This correction eliminates the previous sizable irregularity in the internal contributions at these two positions.

On the basis of the evidence given above, the correct assignments for TMDO and TMPD appear to be those which give increasing contributions of the internal rates from the interior outward and which therefore bring the observed data for all molecules into a consistent picture. If this hypothesis is correct, a more general statement about alkyl chain motion in branched systems can be made: the internal motion increases from the center of the molecule outward regardless of the spacing between branch points.

As stated above, the chemical shift nonequivalences previously observed[43] for the interior positions of TMDO must now be reassigned. However, these differences originate, as before, in the corresponding diastereomers. This reassignment in chemical shift has implications for structural assignments arising from stereochemical configuration. The observed nonequivalences are quit similar for the isopropyl methyl carbons (0.21 ppm) and for the methylene carbons now assigned as C(4) (0.20 ppm), suggesting that both may share a common origin. In the case of nonequivalence arising from stereochemical configuration for higher order stereosequences in polypropylene[48] or in monomer sequences formed in ethylene–propylene rubbers,[49–51] one must now consider that the methylene carbons most sensitive to stereostructure are not necessarily those flanked by meso or racemic methyls (analogous to C(6) in TMDO) but are those methylene carbons $\alpha$ to a branch point and in the position of greatest asymmetry (analogous to C(4) in TMDO). These observations are consistent with $^{13}$C chemical shift trends found in ethylene–propylene rubber[49–51] and for special model copolymers[51]

### Table VII
### Internal Reorientation Rates and Percent Contribution of the Internal Rate to Overall Rate

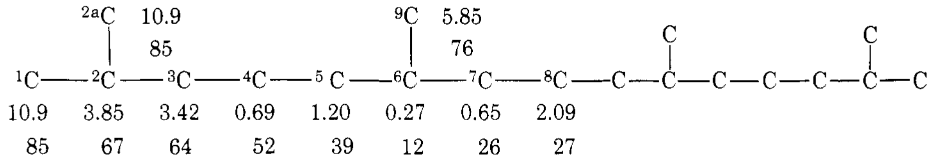
TMDO[a] (310 K)



| 1C | 2C | 3C | 4C | 5C | 6C | 2aC | 7C |
|---|---|---|---|---|---|---|---|
| 9.95 | 3.25 | 2.88 | 1.38<br>1.36 | −0.06 | 0.55 | 9.95 | 6.67 |
| 73 | 46 | 43 | 27 | 0.01 | 13 | 73 | 64 |

$R_0$[b] = 3.746

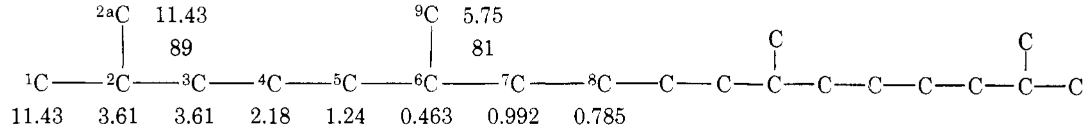
TMPD (310 K)



| 1C | 2C | 3C | 4C | 5C | 6C | 7C | 8C | 2aC | 9C |
|---|---|---|---|---|---|---|---|---|---|
| 10.9 | 3.85 | 3.42 | 0.69 | 1.20 | 0.27 | 0.65 | 2.09 | 10.9 | 5.85 |
| 85 | 67 | 64 | 52 | 39 | 12 | 26 | 27 | 85 | 76 |

$R_0$ = 1.899

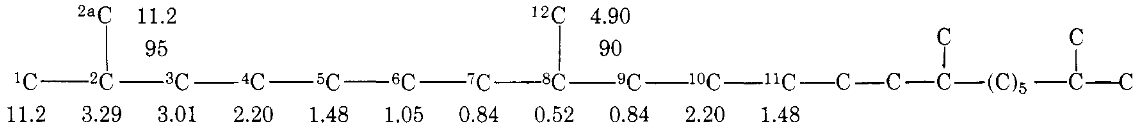
2,6,11,15-TMHD[c] (311-312 K)



| 1C | 2C | 3C | 4C | 5C | 6C | 7C | 8C | 2aC | 9C |
|---|---|---|---|---|---|---|---|---|---|
| 11.43 | 3.61 | 3.61 | 2.18 | 1.24 | 0.463 | 0.992 | 0.785 | 11.43 | 5.75 |
| 89 | 72 | 72 | 61 | 47 | 25 | 42 | 36 | 89 | 81 |

$R_0$ = 1.389
$\tau_0$ assumed to be 72 ps

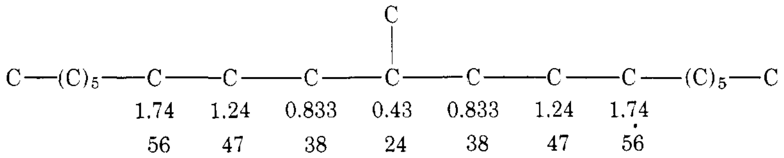
TMHE (310 K)



| 1C | 2C | 3C | 4C | 5C | 6C | 7C | 8C | 9C | 10C | 11C | 2aC | 12C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11.2 | 3.29 | 3.01 | 2.20 | 1.48 | 1.05 | 0.84 | 0.52 | 0.84 | 2.20 | 1.48 | 11.2 | 4.90 |
| 95 | 85 | 84 | 80 | 73 | 65 | 60 | 48 | 60 | 80 | 73 | 95 | 90 |

$R_0$ = 0.561

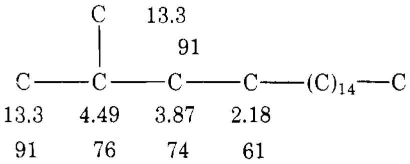
10-Methylnonadecane[c]



| | | | | | | |
|---|---|---|---|---|---|---|
| 1.74 | 1.24 | 0.833 | 0.43 | 0.833 | 1.24 | 1.74 |
| 56 | 47 | 38 | 24 | 38 | 47 | 56 |

$R_0$ = 1.389
$\tau_0$ assumed to be 72 ps

2-Methylnonadecane[c]

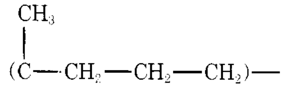


| C | C | C | C | C (branch) |
|---|---|---|---|---|
| 13.3 | 4.49 | 3.87 | 2.18 | 13.3 |
| 91 | 76 | 74 | 61 | 91 |

$R_0$ = 1.389

[a] Numbers associated with each carbon are $R_i$ in units of $10^{10}$ s$^{-1}$ and percent contribution of $R_i$ to $R_i + R_0$. [b] $R_0$ in $10^{10}$ s$^{-1}$ are overall tumbling rates for each compound at the specified temperature. [c] Reference 23.

having pure meso configuration and mixed meso/racemic configurations in a polymer having the structure



$$(\overset{CH_3}{\overset{|}{C}}—CH_2—CH_2—CH_2)—$$

The temperature dependence of $\tau_{eff}$ for the methylene and methine carbons of TMHE conforms to a simple Arrhenius expression over the limited temperature range studied. The apparent activation energies, $\Delta E$, range from 24.7 to 26.8 kJ/mol. If the activation energies of the separate processes contributing to relaxation were different, one might expect a more complicated dependence in ln $\tau_{eff}$ on the reciprocal of the absolute temperature. The calculated overall $\tau_0$ values obtained from the macroscopic viscosity, eq 8, as a function of temperature obey an Arrhenius relationship giving a $\Delta E$ of 28.5 ± 1.4 kJ/mol.

Thus, under the assumption inherent in eq 8 it would appear that the activation energies for overall and internal motions are of similar magnitude. The values appear to be in line with previous studies on $n$-alkanes and bulk polymers.[23]

If one considers the internal rates or percent contribution to the total rate of motion for the end isobutyl segments, the following points emerge: (1) The contribution to the internal rate for terminal methyls changes to a smaller extent with molecular weight than for any other carbon. This is consistent with $n$-alkane studies and reflects the large contribution to relaxation from internal methyl rotation. However, the decay of the autocorrelation function for the end methyl is not totally independent of the overall rotation rate. (2) The percent contributions of the internal rate for carbons C(2) and C(3)

**Table VIII**
**Reorientation Rates for Methyl Carbon CH Vectors about Methyl–Methine Bonds as a Function of Temperature for 2,8,14,20-Tetramethylheneicosane**

| $T$, K | Rate $(\tau_{me}{}^{i})^{-1}$, s$^{-1}$ C(12)–C(8) | Rate $(\tau_{me}{}^{i})^{-1}$, s$^{-1}$ C(2a)–C(2) |
|---|---|---|
| 310 | $4.4 \times 10^{10}$ | $7.9 \times 10^{10}$ |
| 316 | $4.7 \times 10^{10}$ | $8.1 \times 10^{10}$ |
| 322 | $5.9 \times 10^{10}$ | $9.8 \times 10^{10}$ |
| 331 | $6.7 \times 10^{10}$ | $11.4 \times 10^{10}$ |
| 341 | $8.9 \times 10^{10}$ | $14.3 \times 10^{10}$ |
| 352 | $9.2 \times 10^{10}$ | $14.9 \times 10^{10}$ |
| 359 | $12.7 \times 10^{10}$ | $19.2 \times 10^{10}$ |
| $\Delta E$, kJ/mol | 19.2 ± 1.7 | 16.3 ± 1.3 |

**Table IX**
**Reorientation Rates for Methyl Carbon C–H Vectors about Methyl–Methylene and Methyl–Methine Bonds**

| Compd | Rate $(\tau_{me}{}^{i})^{-1}$ (310–312 K), s$^{-1}$ |
|---|---|
| $n$-Eicosane[a] | $13.3 \times 10^{10}$ |
| 10-Methylnonadecane[a] | |
| End methyl | $14.4 \times 10^{10}$ |
| Interior methyl | $5.9 \times 10^{10}$ |
| 2-Methylnonadecane[a] | |
| Isopropylmethyl | $8.8 \times 10^{10}$ |
| End methyl | $12.7 \times 10^{10}$ |
| 2,5,8,11-Tetramethyldodecane[b] | |
| Isopropylmethyl C(1), C(2a) | $6.7 \times 10^{10}$ |
| Interior methyl C(7), C(7a) | $6.7 \times 10^{10}$ |
| 2,6,10,14-Tetramethylpentadecane[b] | |
| Isopropylmethyl C(1), C(2a) | $7.1 \times 10^{10}$ |
| Interior methyl C(9) | $5.6 \times 10^{10}$ |
| 2,6,11,15-Tetramethylhexadecane[a] | |
| Isopropylmethyl C(1), C(2a) | $7.8 \times 10^{10}$ |
| Interior methyl C(9) | $5.2 \times 10^{10}$ |
| 2,8,14,20-Tetramethylheneicosane[b] | |
| Isopropyl methyl C(1), C(2a) | $7.9 \times 10^{10}$ |
| Interior methyl C(12) | $4.4 \times 10^{10}$ |

[a] Data from Lyerla et al.[23] [b] Present work.

**Table X**
**Contribution of Internal Motion for Terminal Methyl, Interior Methyl, and Interior Branch Point**

| Compd | Percent internal contribution Terminal CH$_3$ | Interior CH$_3$ | Interior CH |
|---|---|---|---|
| TMDO | 73 | 64 | ~0 |
| TMPD | 85 | 76 | 12 |
| TMHE | 95 | 90 | 48 |

are essentially identical, indicating a similar type of internal reorientation for the isobutyl segment in all the molecules. Subtracting the contribution of $R_0$ from $R_{eff}$ for the end methyls in TMDO, TMPD, and TMHE and comparing the result with the differences in $R_{eff}$ for the methyl and attached methine (a measure of the methyl rotation rate)[42] suggests the presence of additional internal motions such as rotations about C–C bonds. These motions become more favorable at the chain ends than typical "crankshaft" type motions expected in the chain interior of polymers.

From the temperature dependence of the $\tau_{eff}$ data for TMHE the activation energies, $\Delta E$, of 20.1 ± 1.7 and 20.5 ± 1.7 kJ/mol are obtained for isopropyl and interior methyl carbons, respectively. These values are 4.6 to 6.7 kJ/mol lower than that for the methylene carbon. The methyls in 10-methylnonadecane were found to have $\Delta E$ values of 16.3 and 18.4 kJ/mol for end and interior positions, respectively, while those for the methylenes were 21.4 and 23.0 kJ/mol.[23]

The lower $\Delta E$ values for the methyls can be qualitatively expained in the following way. Reorientation about the three-fold axis requires a minimum change in molecular volume. In a situation where the above motion is the dominant relaxation mechanism, the potential hindering such motion would be the threefold intramolecular potential. If this is the case separation of pure methyl rotation from other motions using eq 7 should give rotational potentials similar to methyl rotation alone.[42] As seen in Table VIII the temperature dependence of the methyl rates for TMHE (Table VIII) leads to activation energies of 19.3 ± 1.7 and 16.3 ± 1.3 kJ/mol for interior and isopropyl methyls, respectively. The activation energy for the interior methyl appears slightly higher and is consistent with greater hindrance to methyl rotation at the interior point of substitution relative to the chain end.

Table VIII contains rates of methyl reorientation calculated from $\tau_{eff}$ of the methyl and attached carbon. All isopropyl type methyls have rates in the range of $6.7 \times 10^{10}$ to $8.8 \times 10^{10}$ s$^{-1}$ while interior rates range from $4.4 \times 10^{10}$ to $6.7 \times 10^{10}$ s$^{-1}$. The interior rates are clearly slower than those of isopropylmethyls indicating hindrance to rotation in the chain interior.

It is interesting to contrast the behavior at the point of methyl substitution in the isobutyl group and at the interior positions. The internal rates decrease for the interior methyl carbons C(7), C(9), and C(12) in TMDO, TMPD, and TMHE. This decrease is consistant with previous[42,53] comparisons of branching in polymers with normal alkanes. On the other hand, the percent contribution of the internal rate increases as shown in Table X. The percent contribution of the internal rate at the interior branch point increases from ~0 in TMDO to 48% in TMHE. These trends reflect the decreased importance of overall reorientation as molecular weight increases. On this basis, TMHE is the best model of the present series for understanding polymer dynamics in methyl-branched alkanes.

In TMHE three resonances are composed of two carbons with accidental chemical shift equivalence. The resonance at 27.95 ppm consists of carbons C(4) and C(10); the resonance at 30.87 ppm consists of carbons C(5) and C(11) and finally the resonance at 37.68 ppm contains carbons C(7) and C(9). It might be expected that carbons 5 and 11 would have different $T_1$'s and the intensity following the 90° pulse in the 180–$\tau$–90 sequence to consist of two exponentials. One would expect carbons C(5) and C(11) to exhibit the greatest difference.

Figure 1 shows a plot of ln $[1 - M(\tau)/M(\infty)]$ vs. $\tau$. Included in the plot are data for the composite resonances C(5), C(11), and C(7), C(9). Also included is the single resonance C(3) as a point of reference. Clearly, the three sets of resonances are described by a single exponential. Similar results were found for the composite resonances C(4) and C(10) as compared with the single resonances C(6) and C(12).

Two theoretical curves are shown in Figure 2. Each represents a pair of carbon resonances of equal intensity. In curve 1 the $T_1$'s differ by 0.4 s while in curve 2 they differ by 0.1 s. Although the curve representing the $T_1$'s in the former case is clearly biexponential, the latter appears exponential. If noise is introduced, one cannot distinguish this composite signal from a single exponential decay of $T_1$ = 0.46 s. At 331 and 352 K the C(5)–C(11) peak is split due to the removal of shift equivalence. The $T_1$'s of the two components differ by less than ~0.2 s. Thus one cannot hope to determine the separate

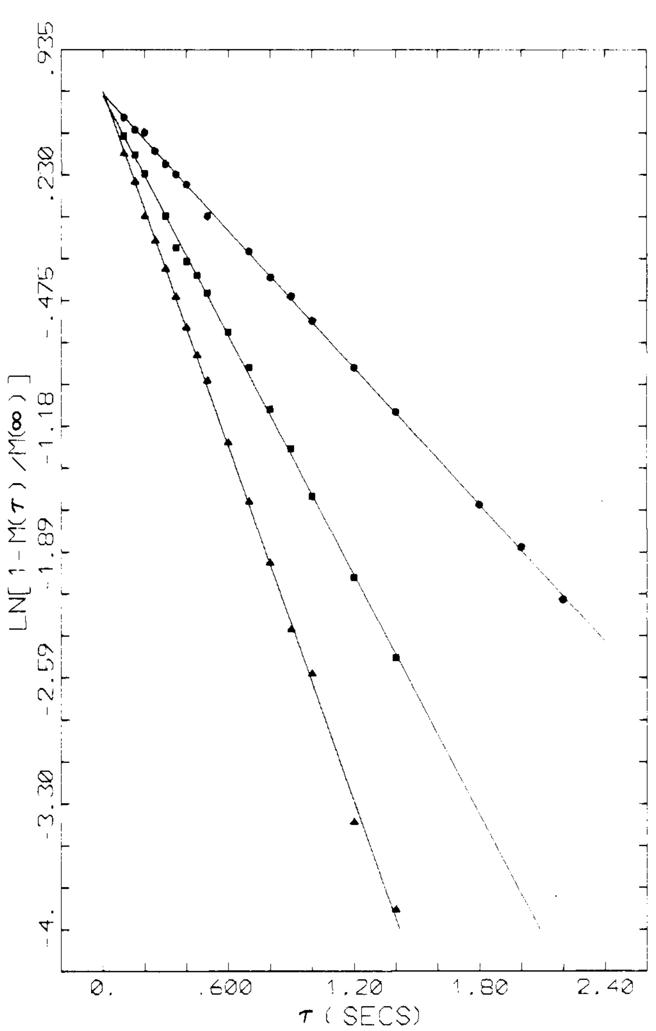


**Figure 1.** ln [1 − $M(\tau)/M(\infty)$] vs. $\tau$ for TMHE at 310 K. Circles, squares, and triangles represent C(3), C(5,11), and C(7,9), respectively.

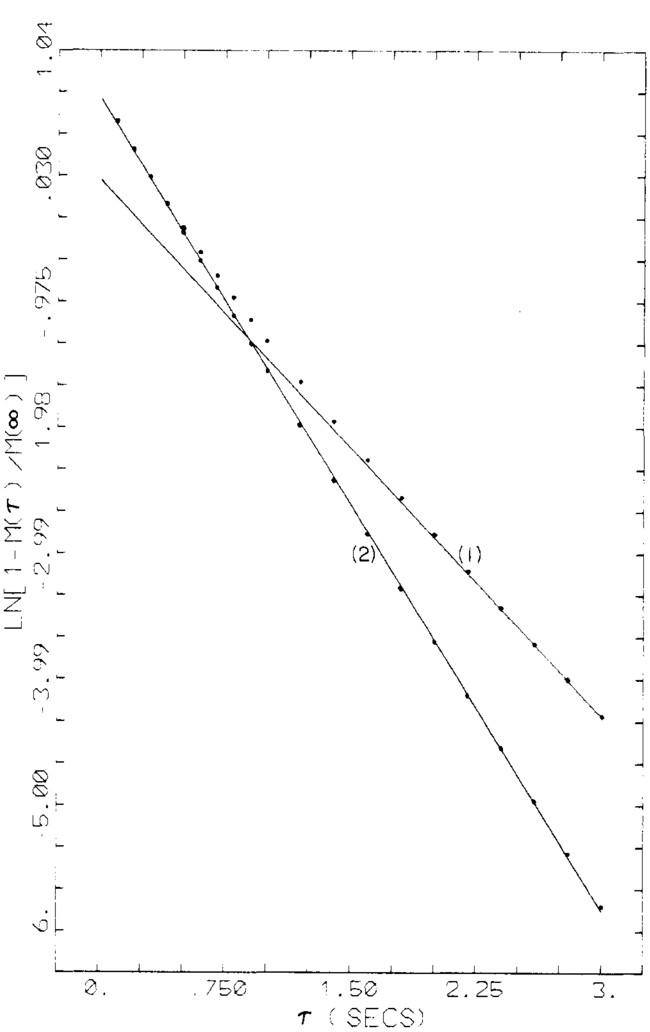


**Figure 2.** Theoretical curves of ln [1 − $M(\tau)/M(\infty)$] vs. $\tau$ for composite resonances of two carbons of equal intensity. In the upper curve 1, $T_{1a}$ and $T_{1b}$ are 0.3 and 0.7 s. In the lower curve 2, $T_{1a}$ and $T_{1b}$ are 0.4 and 0.5 s. The straight lines in the upper and lower curves are for $T_{1b}$ = 0.7 s and the linear least-squares fit of the lower curve 2 data with $T_1$ = 0.46 s.

$T_1$'s from the composite peak. The $\Delta E$ values for C(4)–C(10), C(5)–C(11), and C(7)–C(9) refer to the combined relaxation processes for each pair of carbon atoms. It seems reasonable to conclude that the $T_1$'s of carbons C(7) and C(9) are essentially equal from the following line of reasoning. Carbons C(4) and C(6) of TMDO are resolved and have $\tau_{\mathrm{eff}}$ of 23.3 and 19.6 ps. Carbons C(5) and C(7) of TMHD have $\tau_{\mathrm{eff}}$ values of 38 and 42. As the number of methylenes between the methyl substitution increases, the $\tau_{\mathrm{eff}}$ about the interior methyl substituent converge. As a result one would expect $\tau_{\mathrm{eff}}$ values for C(7)–C(9) to be even closer.

The compounds employed in this study have in the past served as models for polymeric systems reflecting both conformational and configurational structure. The question may be asked as to the suitability of these molecules as models for the dynamics of a macromolecular chain of similar branching. Comparison of the internal rates of TMDO, TMPD, and TMHE show that the internal contribution to interior methine and methylenes increases as expected with molecular weight. However, in the case of TMHE the C(8) position has only a 48% contribution from internal motions. Carbons 9, 10, and 11 show a contribution of 60–80%. The ideal model system would have a repeating segment in the interior whose relaxation is nearly independent of overall motion, the realization of which will require a higher molecular weight than TMHE provides. It must be remembered, however, that ultimately kinematic viscosity data cannot be obtained on a high molecular weight solid, a fact which limits the usefulness of this approach. Consequently, the present data and their trends showing increasing dominance of internal motion do provide an alternate route to understanding macromolecular dynamics. It should be noted, however, that since overall motion in the model compounds has not been totally eliminated, extrapolation of the results to polymeric structures should be approached with caution.

A final point of interest concerns effects of symmetry on relaxation rates. The isopropylmethyls in TMDO and TMPD are nonequivalent and in TMDO the C(4) methylenes are nonequivalent. In all sets of nonequivalent groups, however, relaxation times are identical to within experimental error.

## Summary

Spin-lattice relaxation times and NOE's have been obtained at 310 K for TMDO, TMPD, and TMHE. $\tau_{\mathrm{eff}}$ data for TMHE over a limited temperature range follow an Arrhenius relationship. Activation energies determined from macroscopic viscosity are of comparable magnitude to those obtained from relaxation data. The activation energies are smaller for methyl groups and the corresponding rates of internal motion are fastest for end chain methyls. The internal motion for the isobutyl segment appears to be similar for all pertinent compounds and indicates, as expected, internal motions in addition to main chain type movements responsible for polymer relaxation. Although in TMHE the contribution to internal motion for the interior portion of the chain is sizable, nevertheless, still higher molecular weights are necessary to eliminate the $\tau_0$ contribution. Basic conclusions about methyl-branched chain alkyl motion follow closely those of *n*-alkanes with extensions necessary to describe effects of substitution. The major effect of substitution in the interior of the chain is to slow down the internal rates about the branch points compared to those in corresponding normal alkanes. Although the effect of the number of methylenes between branch points appears minor, additional model compounds not available at present should be designed for future work before firm conclusions can be drawn. Although no rigorous justification of the Lyerla approach is available, the results here appear to be reasonable. The assumption of isotropic motion rather than anisotropic motion may be overly optimistic. However, interpretation in terms of the simple approach appears to be acceptable. Within the assumptions inherent in the simple model, certain shift assignments have been changed and improved. These results are important in light of their applications to polymer microstructure.

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