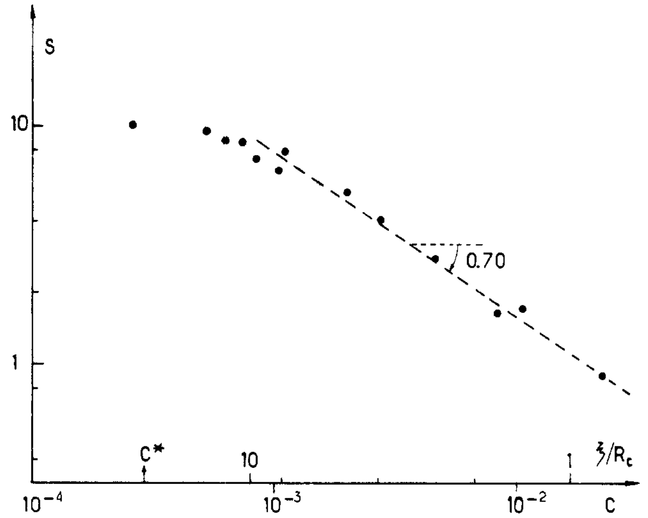

Figure 2. Log s (svedbergs) vs. log c (g/cm^3). For poly(acrylamide) $M_w = 8.2 \times 10^6$ in water–0.1 M NaCl solution in the semidilute concentration range $c > c^*$.

to 0.7 which from relation 10 could correspond to $\nu_D = 0.5$ and $\nu_G = 0.57$.

Conclusion

Forcing the dynamic properties of semidilute solutions into the scaling laws predicted from the blob hypothesis may be in very many cases dangerous. Consistency between the dilute and semidilute results can only be expected if the experiments are performed in similar conditions, i.e., if the range of molecular weights (in the dilute domain) and concentrations (in the semi dilute domain) define equivalent values for the radius of gyration R_G and blob size ξ. Even in good solvents, this generally requires very high molecular weight samples to be used for the study of the semidilute behavior. A more exact consideration of the influence of short distance statistics in the blob hypothesis would be required to describe quantitatively the full concentration dependence.

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Correlation between ^{13}C NMR Chemical Shifts and the Conformation of Polymers. 2. An Improved Method of Calculation

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ABSTRACT: An improved semiempirical method for calculating the ^{13}C NMR chemical shifts of methyl and methylene carbons is presented. The mixture of diastereomers of 2,4,6,8,10,12-hexamethyltridecane (HMTD), ^{13}C enriched on carbon C$_7$, was prepared, and the observed ^{13}C NMR spectrum of HMTD is reported here, together with the assignment of each tetrad resonance of carbon C$_7$. The conformational origin of the stereochemical shifts of polypropylene is qualitatively discussed. It is found that the quantitative agreement between calculated and observed chemical shifts for both the CH$_2$ and CH$_3$ carbons in polypropylene model compounds is improved by taking into account the effect of distortions of the dihedral angles on the γ shielding parameter. The value of γ is found to be considerably smaller for the CH$_2$ carbon than for CH$_3$, suggesting caution in transferring such best-fitting parameters from one carbon to another.

In a previous paper,[1] hereafter referred to as paper 1, a simple statistical treatment was proposed for the calculation of the methyl carbon stereochemical shifts in polypropylene and its model compounds. The method was based on the assumption that the chemical shift of a methyl carbon is determined by the average number of γ gauche and δ syn-axial interactions and on the three-state rotational isomeric model. This method allowed a satisfactory interpretation of the methyl spectrum of 3,5,7,9,11,13,15-heptamethylheptadecane (HMHD); however, in paper 1 we observed that the calculation did not predict wider isotactic bands than syndiotactic bands, as found experimentally, and that the best-fitted γ parameter had a small temperature dependence. We remarked that these facts were likely to be ascribed to the oversimplifications of the three-state model and concluded that the knowledge of the dependence of the γ and δ parameters as functions of the torsional angles was a preliminary requirement in order to fruitfully use more sophisticated statistical models.

Improvements of such semiempirical methods appear necessary for predicting the chemical shifts within (or close to) the limits of current experimental errors. In a recent paper,[2] Tonelli reduced the mentioned defects of our previous calculations[1] by using the Suter–Flory[3] statistical model and disregarding the δ effect; however the overall

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agreement between calculated and experimental chemical shifts of the central methyl carbon of HMHD was not significantly improved. In the present paper we show that the use of the angular dependence of the γ parameter derived from observations on other compounds, coupled with a realistic statistical model,[3,4] significantly improves the agreement between calculated and observed chemical shifts both for the methyl and for the methylene spectrum of polypropylene model compounds.

In order to clarify the ^{13}C NMR methylene spectra of polypropylene, and also to assess the validity of our method for predicting CH_2 chemical shifts, the diastereomers of 2,4,6,8,10,12-hexamethyltridecane (HMTD), having the central C_7 carbon 90% ^{13}C enriched, were prepared, and the ^{13}C spectrum of the HMTD diastereomer mixture was recorded. The preparation of HMTD and the assignment of the carbon C_7 resonances are described in the following sections.

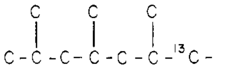
Experimental Section

Materials. Two samples of the 2,4,6,8,10,12-hexamethyltridecane diastereomer mixture were prepared, differing for the partial resolution of the starting material. The two samples are indicated as I and II, and here we describe the preparation of sample II. 2,4-Dimethylpentanoic acid (0.16 mol) partially resolved ($[M]^{26}{}_D$ −5.86 in CH_3Cl) by crystallization of the dehydroabietylammonium salt[5] was reduced with $LiAlH_4$ in diethyl ether to 2,4-dimethylpentanol. This was transformed into the corresponding bromide with dibromotriphenylphosphorane in CH_3CN as described in the literature.[31] Crude 1-bromo-2,4-dimethylpentane, dried on $CaSO_4$, was fractionally distilled, and 15 g of pure (99% by GLC) product was collected (62% yield based on the acid).

To the corresponding Grignard reagent prepared in 200 mL of anhydrous diethyl ether, we added 0.1 mol of acetaldehyde at 0 °C. The reaction mixture was stirred at room temperature overnight and then hydrolyzed with aqueous NH_4Cl. The collected organic layer was repeatedly washed with water and dried on $CaSO_4$, and after filtration the solvent was evaporated. The reaction product (4,6-dimethyl-2-heptanol) without further purification was reacted with 0.09 mol of dichlorotriphenylphosphorane in CH_3CN. By fractional distillation of the crude 2-chloro-4,6-dimethylheptane, 6 g of product (90% purity by GLC) was collected (yield 44%); 2-chloro-4,6-dimethylheptane dissolved in 30 mL of anhydrous *n*-pentane was dropped during 30 min into a stirred suspension of 0.2 mol of Li sand kept at 0 °C in a nitrogen atmosphere. After 4 h the reaction vessel containing the Li alkyl solution was cooled at liquid nitrogen temperature and evacuated at 10^{-5} mmHg, and 0.01 mol of $^{13}CO_2$ (90% ^{13}C enriched) was introduced. The mixture was warmed to room temperature and vigorously stirred for 1 h. The atmospheric pressure was restored with nitrogen, the solvent evaporated, 30 mL of benzene added, and the solution refluxed overnight. The reaction mixture was then hydrolyzed by dropping in 100 mL of stirred HCl-acidified methanol, diluted with 500 mL of water, and repeatedly extracted with diethyl ether. The organic layer was washed to neutrality and dried, and the solvents were completely evaporated in vacuo (10 mmHg) at 60 °C. To the residue, containing the desired 2,4,6,8,10,12-hexamethyl-7-tridecanol and dissolved in 25 mL of cyclohexane, we added 0.5 mL of 1,2,4-trichlorobenzene, and a catalytic C–OH hydrogenolysis was performed (140 °C; P_{H_2} 50 atm; time 24 h) in the presence of 1 g of 10% Pd on charcoal.

After filtration and elimination of the solvent, the organic residue contained 4% (by GLC) 2,4,6,8,10,12-hexamethyltridecane, 90% ^{13}C enriched on C_7. The absence of functional groups (OH, COOH) was checked by IR analysis.

GC–MS Analysis. The mass spectrum of ^{13}C enriched hexamethyltridecane was scanned from *m/e* 20 to 300. Figure 1 shows only the spectral range *m/e* 100–210. In fact the presence of several fragments with even mass number starting from *m/e* 142 allows identification of product



$$C-\overset{\overset{C}{|}}{C}-C-\overset{\overset{C}{|}}{C}-C-\overset{\overset{C}{|}}{C}-{}^{13}C-$$

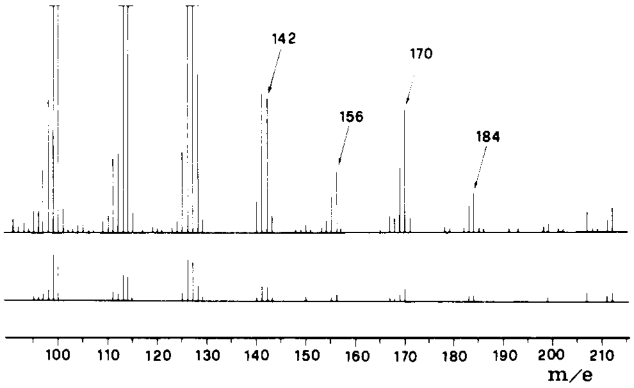


Figure 1. Mass spectrum of sample II of HMTD.

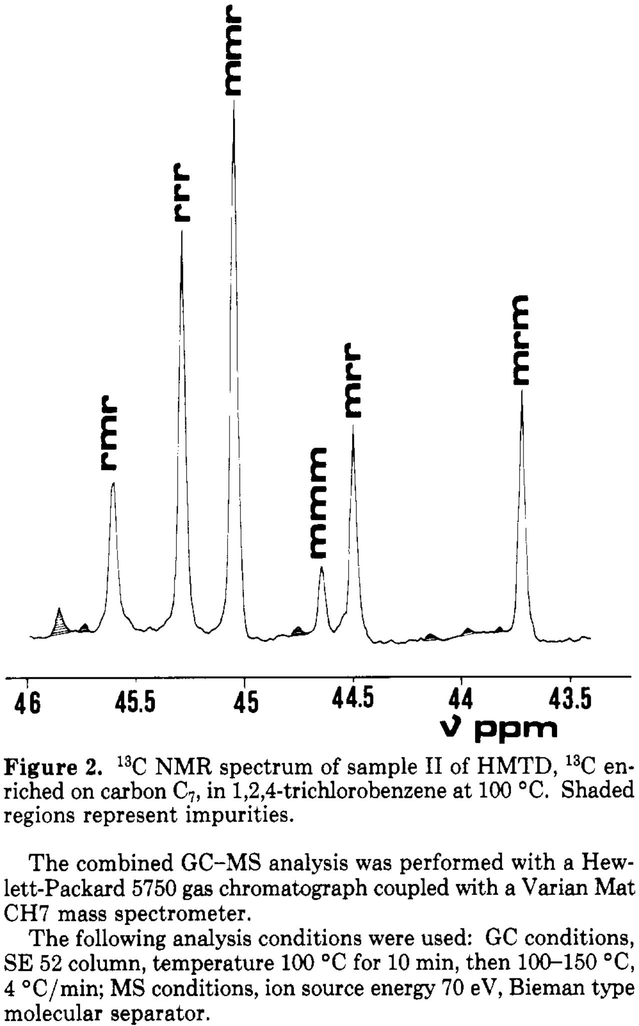


Figure 2. ^{13}C NMR spectrum of sample II of HMTD, ^{13}C enriched on carbon C_7, in 1,2,4-trichlorobenzene at 100 °C. Shaded regions represent impurities.

The combined GC–MS analysis was performed with a Hewlett-Packard 5750 gas chromatograph coupled with a Varian Mat CH7 mass spectrometer.

The following analysis conditions were used: GC conditions, SE 52 column, temperature 100 °C for 10 min, then 100–150 °C, 4 °C/min; MS conditions, ion source energy 70 eV, Bieman type molecular separator.

^{13}C NMR Spectra. On account of ^{13}C selective enrichment, ^{13}C NMR analysis was performed without isolating the pure compound. The spectrum of sample I was measured with an HX-90 Bruker spectrometer operating at 22.63 MHz in the PFT mode. The sample was dissolved in 1,2,4-trichlorobenzene by adding 1% of hexamethyldisiloxane as an internal reference, and the temperature of the probe was 140 °C. The spectrum of sample II was recorded at 100 °C with an HX 270 Bruker spectrometer operating at 67.88 MHz.

Assignment of the HMTD Resonances

In Figure 2 we show the expanded ^{13}C NMR spectrum of sample II of HMTD, which was measured at 100 °C and is somewhat better resolved than that of sample I. However, for consistency with previous work done in this laboratory, in Table VII we shall report the chemical shifts observed for sample I at 140 °C. The relative intensities

Table I
Relative Intensities of the Six Carbon C_7 Resonances in Samples I and II of HMTD and Assignment to the Six Diastereomers

peak	sample I	sample II	diastereomer assigned
a	12.0	12.7	*rmr*
b	19.9	24.9	*rrr*
c	28.9	30.5	*mmr*
d	7.0	5.3	*mmm*
e	18.6	12.6	*mrr*
f	13.6	14.0	*mrm*

of the six peaks, indicated with letters a to f in order from low to high field, are given in Table I.

In order to assign the carbon C_7 resonances to the various diastereomers of HMTD one must take into account the following facts. (i) Due to the partial resolution of the starting material (2,4-dimethylpentanoic acid), the following relationship holds between the concentrations of the six possible diastereomers

$$(mmr) + (mrm) + (rrr) > (mmm) + (mrr) + (rmr)$$

Moreover, the three concentrations on the left are expected to increase (and the three on the right to decrease) in sample II with respect to sample I, due to a greater resolution of the starting compound. (ii) Diastereomers *mmr* and *mrr* are degenerate with *rmm* and *rrm*, respectively. Hence their concentrations are approximately equal to the sum of the concentrations of diastereomers *mrm* and *rrr* and of diastereomers *rmr* and *mmm*, respectively. (iii) In previous preparations of similar compounds it was observed[6] that, in the step of C–OH hydrogenolysis, formation of syndiotactic dyads in the central part of the compounds is favored with respect to isotactic dyads (perhaps owing to greater thermodynamical stability of syndiotactic dyads[7]). That is, given the configurations of carbons C_4 and C_{10}, those configurations of carbons C_6 and C_8 are preferred which bring about *r* pair configurations. Hence concentrations of diastereomers *rmr* and *rrr* are expected to be greater, respectively, than concentrations of *mmm* and *mrm*.

The following assignment was then derived from all the above considerations and from the observed intensities listed in Table I. Peaks c and d are readily assigned to diastereomers *mmr* and *mmm*, which must correspond respectively to the highest and lowest intensity. As expected, the concentration of *mmr* is greater in sample II than in sample I, while the concentration of *mmm* is smaller in sample II. For the same reason we must expect an increase of concentration in sample II for *rrr* and *mrm* and a decrease for *mrr* and *rmr*. We observe that resonance b is the second most intense, after peak c (*mmr*), among those whose intensity is greater in sample II, and is therefore assigned to diastereomer *rrr*. On the other hand, resonance e is the most intense one among those whose intensity is greater in sample I, hence it is assigned to *mrr*. There is some uncertainty regarding the assignment of the two remaining peaks to diastereomers *mrm* and *rmr* on the basis of the relative intensities. In fact the concentration of *mrm* should be greater in sample I than in sample II, and the opposite should occur for diastereomer *rmr*, while a small increase in sample II is observed for both resonances a and f. We feel that the intensities of peak a in sample II and of peak f in sample I may be somewhat overestimated; for example, Figure 2 shows that resonance a is significantly wider than the other five, indicating that some impurity may contribute to the estimated intensity. For these reasons we assigned resonance a to *rmr* and resonance f to *mrm*.

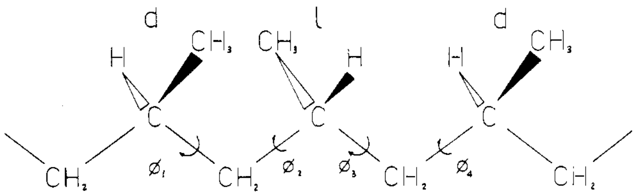


Figure 3. Two racemic dyads (*dld*) of polypropylene in the fully extended conformation (*TT*/*TT*).

Table II

ll	*ld*	*dl*	*dd*
TG	*TT*	*GG*	*TG'*
G'T	*G'G'*	*TT*	*GT*

Furthermore, we may remark that, having assigned the resonances corresponding to diastereomers *mmr*, *mmm*, and *rrr* without any doubt, any assignment of the other three resonances different from that just described would contradict the reasonable hypothesis that the effects of the configurations of the two side dyads on the chemical shift of the central methylene carbon are approximately additive, so that the signal of *mmr* is intermediate between those of *mmm* and *rmr*, and the signal of *mrr* is intermediate between those of *rrr* and *mrm*.

Conformational Origin of the Stereochemical Shifts

In the following we show that the effects of the configuration of the neighboring units on the chemical shift of a given methyl (or methylene) carbon can be qualitatively rationalized on the basis of the γ effect and of the major conformational characteristics of the polypropylene chain.

The notation used by Boyd and Breitling[4] to describe the conformation and the stereochemical configuration of polypropylene will be adopted throughout this article. Figure 3 shows a schematic representation of a chain segment. We follow Boyd and Breitling in using the symbols *l* and *d* to indicate the (conventionally defined) configuration of a given carbon, rather than + and − as proposed recently by Zambelli et al.,[5] in order to avoid confusion with the signs + and − indicating conformational distortions.

The well-known main conformational features of the polypropylene chain are the following:[3,4,8,9] (a) An isolated dyad can assume two equiprobable conformational states (indicated in Table II), besides small contributions of less stable states. Each bond may assume mainly two conformations; for example, the bond preceding a carbon *l* may take the conformations trans *T* and gauche *G*, the third one (*G'*) being much less probable. (b) Couplings of type gauche/trans ...*G*/*T*..., ...*T*/*G'*..., etc., between two adjacent dyads are slightly favored over couplings of type ...*T*/*T*... and highly favored over couplings of type ...*G*/*G'*... (due to a pentane interference).

Therefore, if we consider an isolated dyad (2,4-dimethylpentane), all methyls[29] have equal probabilities of being in the gauche conformation with respect to the γ methine: $P(1,TG) = P(1,G'T)$ for a meso *ll* dyad and $P(1,TT) = P(1,GG)$ for a racemic *dl* dyad, etc. If we now add a second dyad (2,4,6-trimethylheptane), since couplings ...*T*/*T*... are favored with respect to ...*G*/*G'*..., the gauche probability (P_g) in the first dyad increases for the second methyl and for the first methyl having configuration opposite to the second methyl and decreases for the first methyl having the same configuration as the second methyl (and for the methylene): $P(1,G'T) > P(1,TG)$ in terms of a meso *ll* dyad and $P(1,TT) > P(1,GG)$ in terms of a racemic *dl* dyad, etc.

This is then the first-neighbor configurational effect. Rule b on the dyad/dyad couplings also determines the sign of (smaller) second-, third-,... neighbor effects. In fact, addition of a third dyad to *lll* (giving *meso*-2,4,6,8-tetramethylnonane) produces the first neighbor effect of decreasing $P(2,TG)$, and since the state TG of the first dyad is favorably coupled only with TG of the second one, the decrease of $P(2,TG)$ causes a further decrease of $P(1,TG)$. If the third dyad is added to *ldl* (giving *rac*-tetramethylnonane), there is a decrease of $P(2,GG)$ which in turn yields a decrease of $P(1,TT)$. In both cases, making the third methyl *l* causes a decrease of the gauche probability for the first methyl *l* independently of the configuration of the second methyl. Opposite effects would have been produced of course by addition to *lld* or to *ldd*, increasing respectively $P(2,TT)$ and $P(1,TG)$ or $P(2,GT)$ and $P(1,TT)$.

Obvious similar considerations allow one to extend to *any* separation the general statement that a methyl of a given configuration produces a downfield shift (decrease of P_g) for a methyl carbon of the same configuration. As a consequence, the signals corresponding to the configurations *...llll*llll...* (or *...mmmm*mmmm*) and *...llld*lll...* (*mmmr*rmmm*) are the extremes of the spectrum. These qualitative considerations are in agreement with the observations of Zambelli and Gatti,[10] who found that addition of a methyl group in a chain, at any distance from the observed methyl carbon, always produces an upfield or a downfield shift according to whether the two methyls have opposite or equal configuration.

Similar arguments allow one to rationalize also the methylene spectrum, if in this case too the chemical shift is determined by the probability that the CH_2 observed be in gauche conformation with respect to the γ methines. It can be first observed that the changes of P_g for a CH_2 of a given dyad are opposite to the sum of the changes of gauche probability between the first methyl forming that dyad and its γ methine in the preceding dyad and between the second methyl and its γ methine in the following dyad.[11] It follows that in 2,4,6,8-tetramethylnonane the mutual second-neighbor interaction between the two external dyads has the effect of decreasing or increasing, on both sides, the P_g of the central CH_2 depending on whether the central dyad is meso or racemic. Hence the total splitting is of the order of magnitude of four times the second-neighbor effect. Addition of further dyads on each side produces first-, second-, ... neighbor effects on the central CH_2 (opposite to the effects on the methyls) so that there is considerable overlap between the *m* and the *r* bands, the latter lying at higher field. (This is in contrast with the description, based on earlier simplified calculations and on low resolution data,[12] according to which the *m* band is at higher field than the *r* band, but is not in contrast, as we shall see, with the fact that the signal of isotactic polypropylene is at higher field than the syndiotactic signal.) The signals corresponding to the configurations *...llld*dlll...* (*...mmrm*rmm...*) and ...llll**dddd...* (*...mmmr*mmm...*) are respectively the low and high field extremes of the methylene spectrum.

These are qualitative arguments. Obviously, quantitative prediction of the spectrum requires explicit calculations based both on a statistical model as accurate as possible and on the correct estimate of the shielding effects associated with each conformational state.

Statistical Model

In paper 1 we adopted the three-state rotational isomeric model of polypropylene, in which three conformations (trans, gauche, and gauche′) are possible for each bond of the chain. The probability of finding a given bond in one of the three states was calculated following essentially the work of Boyd and Breitling.[4] However, on the basis of conformational energy computations it was shown by these authors[4] and by Suter and Flory[3] that the three-state model provides only a crude approximation and that a five-state rotational isomeric model is needed for a realistic representation of the conformational characteristics of the polypropylene chain.

Therefore, for the calculations of the chemical shifts presented in this paper, we adopted the model of Boyd and Breitling.[4] According to these authors each bond of the chain may assume five conformational states: the usual T, G, and G' plus a distorted trans (T_{-}, $\phi \sim 140°$) and a distorted gauche (G_{+}, $\phi \sim 97°$). The distortions arise when a syn-axial interaction (or "pentane interference") takes place either within a dyad or at the junction of two dyads. A dyad *ll*, for example, can assume the following conformational states, each corresponding to an energy minimum: $G'T$, $G'_{-}T$, $G'_{-}G$, TT_{-}, $T_{+}G'$, and GG_{+}, as well as the symmetrical ones TG, TG_{+}, etc. The state $G'T$ is the most stable one, while $G'_{-}T$ is the deformation of $G'T$ due to a dyad/dyad syn-axial interaction and is therefore coupled only with TG (helix inversion $TG/G'_{-}T$). The two states $G'_{-}G$ and TT_{-} are associated with a syn-axial interaction within the dyad (E_{ω}), and finally the two states $T_{+}G'$ and GG^{+} are the least stable ones, implying a syn-axial and a gauche interaction ($E_{\omega} + E_{SK}$). Analogously one defines the conformational states of dyads *dl*, etc. If one disregards the angular distortions, this model is reducible to the three-state model used in paper 1, with the exception that such states as (TT_{-} and $T_{+}T$) and ($G'_{-}G$, $G'G_{+}$) in dyad *ll* and the helix inversion ($...G/G'_{-}...$, $...G_{+}/G'...$) are counted twice. In order to maintain a correspondence with the values of the parameters E_g, E_{SK}, and E_{ω} used in paper 1, we then subtract a term $RT \ln 2$ from the energy of the most stable state ($G'T$, etc.). Actually, one can interpret the term $RT \ln 2$ as an estimate of the entropy contribution stabilizing the wider minimum $G'T$ with respect to the less stable states. For a given set of values of E_g, E_{SK}, and E_{ω}, the model used in this work is, energetically, only slightly different from that of paper 1, in the sense that the least stable states ($T_{+}G'$, GG_{+}, etc.) have halved probabilities.

The five-state rotational isomeric model of polypropylene was refined by Suter and Flory;[3] the major difference with respect to the previous work of Boyd and Breitling[4] is that they took into account the entire energy surface, rather than only the minima in the conformational energy. As a consequence, in the model of Suter and Flory each of the five states corresponds to the weighted average over a conformational domain, and the three statistical weights which define the model are functions not only of three energy parameters (approximately corresponding to those of Boyd and Breitling's) but also of three entropy parameters. Suter and Flory[4] found that the parameters derived from their energy calculations satisfactorily reproduced the data of Suter, Pucci, and Pino,[7] who determined the epimerization equilibria for the diastereomers of 2,4,6,8-tetramethylnonane and 2,4,6,8,10-pentamethylundecane.

On the basis of the calculations of paper 1 we were unable to determine a unique set of energy parameters (and of the parameter γ) by best fitting the methyl carbon chemical shifts, but we could restrict their values within a range of about 0.2–0.3 kcal/mol; this range included the values corresponding to the energy parameters given by Suter and Flory.[4] Thus we picked[1] two representative sets of E_g, E_{ω}, and E_{SK}, which reproduced the experimental methyl chemical shifts of HMHD with approximately equal accuracy; the second of such energy sets was chosen as an intermediate among the various sets given by Suter and Flory (apart from differences in the entropy contributions). Subsequent to the publication of paper 1, we checked the validity of the statistical method used by us against the thermodynamical data of Suter, Pucci, and Pino.[7] It was found that when using set I of the energy parameters the concentration of iso tetramethylnonane at a low temperature is not adequately reproduced, hence we discard this set of parameters. On the contrary, set II reproduces the thermodynamical data just about as accurately as the best-fitting three-state model of Suter, Pucci, and Pino[7] or the model of Suter and Flory.[4] This is not too surprising, since set II is intermediate among the energy values given by Suter and Flory, although it must be observed that there are some significant differences between the two models.[13]

In the present work we shall adopt the model of Boyd and Breitling, as described above, using set II of E_g, E_{SK}, and E_ω, without attempting to optimize these parameters. The present description of the polypropylene chain is not meant to represent an improvement over Suter and Flory's one. As shown in the next section, it was chosen mainly because it would allow us to examine the relationship between the intramolecular interactions in a given minimum energy conformation and the associated shielding effects. For comparison, in the Results section we shall also present some calculations carried out using Suter and Flory's model.

Shielding Effects

In paper 1 the methyl carbon chemical shifts were calculated using the relationship

$$\nu = \nu_0 + \gamma P_g + \delta P_\omega \qquad (1)$$

where the parameters γ and δ correspond to shielding and deshielding effects associated, respectively, with γ gauche and δ syn-axial interactions, as observed experimentally in several rigid compounds.[14-18] There is no good reason for neglecting the δ effect, although it plays a small role in flexible molecules.

According to the Boyd–Breitling model described in the previous section, a given methyl carbon can assume five different values of the dihedral angles formed with its γ methines: in order to avoid confusion between the names indicating the chain conformation and the dihedral angles formed by the methyl carbons, we shall indicate the latter with lower-case symbols, namely t, g, g', t_-, and g_+. Therefore, the shielding effects corresponding to these conformations must be established in order to apply the refined model.

With this purpose in mind, we have examined the correlation between conformation and ^{13}C chemical shifts of the four stereoisomers of 1,3,5,7-tetramethylcyclooctane (TMCO). The conformation of TMCO had been previously elucidated by means of energy calculations and correlated with the vicinal proton coupling constants.[19] While the detailed results of this work will be presented elsewhere, we wish to summarize the conclusions of interest in this article:

(a) The methyl spectrum of TMCO can be fitted with reasonable accuracy by assuming a linear relationship between the chemical shift of a methyl in a given conformer and the nonbonded interaction energy (E_β) between that CH$_3$ group and the CH$_2$ groups in the β position with respect to it: a larger (positive) E_β corresponds to a downfield shift. The experimental chemical shifts and the corresponding values of E_β are given in Table III.

Table III
Experimental Chemical Shifts[20] for the Methyl Carbons of the Four TMCO Stereoisomers and the Corresponding Nonbonded Energy E_β

methyl config	ν,[a] ppm	E_β,[b] kcal/mol
mmmm	26.91	0.67
rrrr	24.51	0.38
mrmr	25.70	0.48_5
*rm*mr*	25.71	0.53
*mm*rr*	26.02	0.55
*mr*rm*	24.65	0.38

[a] Relative to internal Me$_4$Si in C$_6$D$_6$ solutions at room temperature. [b] Average between the values of the low energy minima, computed using Warshel and Lifson's consistent force field (ref 21 and 19). The values of E_β are given as the difference with respect to the value calculated for the methyls of 1-*cis*-3-*cis*-5-trimethylcyclohexane, taken arbitrarily as the reference.

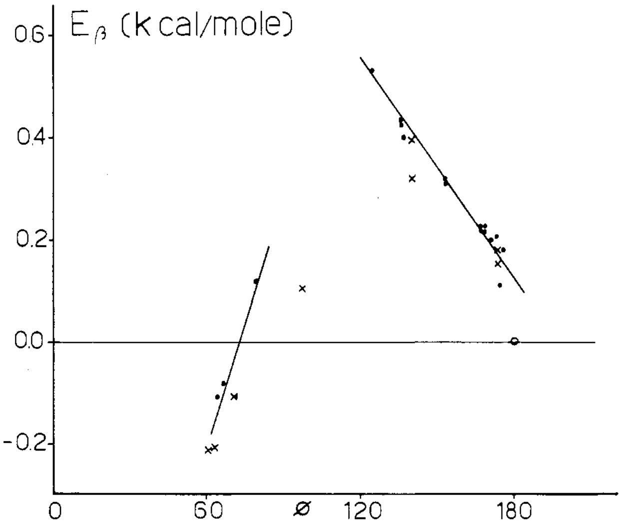


Figure 4. Nonbonded energy CH$_3$···CH$_2$ (E_β) plotted vs. the dihedral angle C–C$^\alpha$–C$^\beta$–C$^\gamma$: (●) TMCO, (×) TMH, (○) TMCH. Conventionally, the value of E_β for TMCH has been set equal to zero.

(b) While in principle E_β depends primarily on the torsional angles H–C–C$^\alpha$–C$^\beta$ and C–C$^\alpha$–C$^\beta$–H, in practice the angle H–C–C$^\alpha$–C$^\beta$ corresponds almost always to staggered conformations, so that it is possible to plot E_β as a function of the dihedral angle C–C$^\alpha$–C$^\beta$–C$^\gamma$ only. The plot has approximately the shape of two straight lines, with a maximum around 120° (see Figure 4).

(c) A behavior of the chemical shift similar to that exhibited by E_β, with downfield shifts corresponding to distortions from the trans conformation, seems necessary for explaining not only the relative positions of the TMCO methyl signals but also the range of frequencies relative to Me$_4$Si (24.5–26.9 ppm), compared, for example, with 23.1 ppm for the equatorial methyls of 1-*cis*-3-*cis*-5-trimethylcyclohexane[14] (TMCH), or with the range displayed by polypropylene itself. We notice that deshielding effects due to syn-axial interactions can be excluded for the methyls of TMCO.[19]

The hypothesis of a correlation between chemical shift and the energy E_β was suggested to us by the work of Beierbeck and Saunders,[22-25] who have recently proposed a new interpretation of the γ effect. According to these authors a β_{HC} deshielding effect occurs for each syn-axial pairing of an H–C bond of the observed carbon and an H–C$^\beta$ of a carbon in the β position. Then the γ effect would simply arise from the removal of one such pairing when a gauche C–C$^\alpha$–C$^\beta$–C$^\gamma$ conformation occurs. For the

Table IV
Dihedral Angles and the Corresponding Values of E_β for *the Central Methyl Group in Some Minimum Energy* Conformations of TMH[a]

		dyad 1		dyad 2	
conformation[b]	E_{total}, kcal/mol	CH-CH$_2$-CH-CH$_3$, deg	E_β,[c] kcal/mol	CH$_3$-CH-CH$_2$-CH, deg	E_β, kcal/mol
$G'T/G'T$	0	−61.1	−0.214	173.8	0.184
$G'T/TG$	0.27	−63.1	−0.210	63.1	−0.214
TG/G'_-T	1.21	−174.3	0.153	140.1	0.339
$G'T/G'_-G$	1.63	−70.9	−0.111	140.0	0.397
$G'T/G'G_+$	1.84	−60.2	−0.223	171.9	0.201
TT_-/T_+T	4.31	−97.2	0.155	97.2	0.155

[a] Computed utilizing Warshel and Lifson's force field (ref 21). [b] Referred to the conventional configuration *lll*. [c] Values relative to E_β of TMCH, taken as zero.

case of deviations from the staggered conformations, Beierbeck and Saunders[24] tentatively proposed a cosine dependence of β_{HC} on the angular distortion from a perfect pairing; however, we found that such a dependence did not reproduce the TMCO methyl spectrum and decided to take the total $CH_3 \cdots CH_2$ repulsion energy as a measure of the β_{HC} term. Hence we do not imply a physical meaning in the observed correlation.

The plot of Figure 4 provides, at least approximately, the behavior of the γ effect as a function of the $C–C^\alpha–C^\beta–C^\gamma$ torsional angle ϕ. We observe that it has been reported in the literature that a carbon in the trans conformation is shielded relative to one having a dihedral angle ϕ near 120° with respect to a carbon or a heteroatom.[18,26,27]

From Figure 4 it also appears that the central methyl of 2,4,6-trimethylheptane (TMH) shows a behavior of E_β vs. ϕ similar to that of the TMCO methyls. In Table IV we present the values of ϕ and E_β for a few conformational states of TMH. These results, on the basis of the correlation between chemical shift and E_β found in TMCO, indicate that a methyl carbon in the distorted state t_- is deshielded with respect to state t, while in state g_+ it is approximately as shielded as in t. Moreover, since syn-axial interactions may cause significant deformations of the dihedral angles, even in rigid compounds where δ deshielding effects are observed, the shielding angular dependence here assumed might offer a simple explanation of the δ effect, namely that it represents the decrease of the γ effect due to the conformational distortion from g toward g_+.[28]

On the basis of the above considerations, we assigned the following shielding parameters γ_i to the five conformational states of a methyl carbon: 0 to t (taken as the reference) and to g_+, γ to g and g', and $-{}^1/_2\gamma$ to t_-. Moreover no specific term for the δ effect was considered, since it is assumed to be included in the γ term. The expression of the chemical shift calculated for a methyl of a certain stereoisomer is therefore given by

$$\nu = \nu_0 + \sum_{i=1}^{5} \gamma_i P_i \qquad (2)$$

where P_i is the probability of state i (on both sides of the chain) for that methyl.

Results

The Methyl Spectrum of HMHD. In paper 1 it was shown that the experimental chemical shifts of the central methyl of the stereoisomers of HMHD were equally fitted by the corresponding values calculated for HMHD and for 2,4,6,8,10,12,14-heptamethylpentadecane (HMPD). In fact, the small calculated heptad splitting due to the terminal ethyl groups did not affect appreciably the position of the resonances corresponding to the stereoisomers actually observed, which lie at the center of each theoretical heptad band. Hence for simplicity here we calculate the methyl spectrum of HMPD, using the model outlined in the previous sections and fitting the parameter γ to the experimental frequencies of HMHD.

In Table V we compare the mean square error and the least-squares fitted γ obtained at three different temperatures with the present method with those of other calculations. The calculated chemical shifts and their errors are listed in Table VI. The results show a clear improvement with respect to the previous calculations at all temperatures. Moreover the parameters γ and ν_0 are now practically independent of the temperature, so that the changes of the signal positions with temperature can be explained in terms of changes of conformer populations only. Although γ and ν_0 should be considered just as best-fitting parameters, we observe that the numerical value of γ is close to the results of regression analyses on many compounds;[25] the value of ν_0, compared with the experimental chemical shift of TMCH, 23.1 ppm relative to Me_4Si,[14] seems reasonably consistent with the positive value of E_β for the conformation t.

In the last column of Table V we report the results obtained by applying eq 2 to the conformer probabilities computed using the method of Suter and Flory (using eq 43 of ref 3). Although the values of the dihedral angles differ by about 10–15° from those of Boyd and Breitling's model, we used the same values of γ_i, since the dependence of γ on the dihedral angle is only approximately known. The agreement with the experimental chemical shifts is almost as good as that with the model adopted by us, indicating that the improvement with respect to the calculations of ref 2 is due to accounting for the angular dependence of γ rather than to differences between the two models.

The Methylene Spectrum of 2,4,6,8,10,12-Hexamethyltridecane (HMTD). As we have seen earlier, the methylene carbon spectrum could be interpreted in terms of conformational changes, if the γ effect is the sole major conformational factor determining the chemical shift. On the basis of this assumption, Tonelli[2] has calculated the chemical shifts of the methylenes 8 and 10 of HMHD, taking the parameter γ equal to the value for the methyl carbon. Since the methylene spectrum of HMHD is not known, we have taken into consideration for our calculations the central CH_2 of HMTD, whose spectrum has been reported and assigned in one of the previous sections.

Table V
Mean Square Error (10^{-2} ppm^2) and Parameter γ (ppm) of Various Calculations on the HMHD Methyl Spectrum

	ref 1, set I		ref 1, set II		ref 2		this model, set II, eq 2		Suter–Flory, using eq 2	
T, °C	MSE	γ	MSE	γ	MSE	γ	MSE	γ	MSE	γ
20	0.24	−7.70	0.34	−5.19	0.43	−5.4	0.19	−4.87	0.22	−5.43
80	0.27	−8.07	0.34	−5.47	0.25	−5.4	0.17	−4.85	0.18	−5.55
140	0.11	−8.44	0.19	−5.74	0.13	−5.2	0.07	−4.81	0.09	−5.59

Table VI
Chemical Shifts of the Central Methyl of the HMPD Stereoisomers, Calculated by Means of Equation Their Error ($\nu_{calcd} - \nu_{obsd}$) Relative to the Experimental HMHD Values[1,6,10]

	T = 20 °C		T = 80 °C		T = 140 °C	
config	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
mmmm	19.280	−0.087	19.591	−0.067	19.777	−0.021
mmmr	19.002	0.024	19.343	−0.013	19.576	−0.006
rmmr	18.714	0.027	19.097	0.032	19.379	−0.009
mmrr	18.627	0.059	18.887	0.060	19.077	0.034
mmrm	18.464	0.004	18.727	0.029	18.936	0.044
rmrr	18.302	0.025	18.630	0.014	18.882	−0.010
rmrm	18.114	−0.001	18.462	−0.020	18.741	−0.021
rrrr	17.800	−0.034	18.117	0.002	18.373	0.021
mrrr	17.554	0.011	17.921	0.011	18.224	0.001
mrrm	17.268	−0.027	17.710	−0.049	18.071	−0.033
γ	−4.867		−4.853		−4.806	
ν_0	24.230		24.338		24.341	

It has been observed[22] in rigid compounds (decalin and cyclohexane derivatives) that a gauche conformation induces, besides the shielding effect on the two γ carbons, also a deshielding effect on the two central carbons. This contribution, called the β_{CC} term by Beierbeck and Saunders,[22] is of the order of 1.5 ppm, so that it could in principle affect significantly the CH_2 spectrum of flexible chains. However, considering the most stable states of a dyad, it can be seen that a CH_2 is always involved in two β_{CC} contributions, independent of the dyad configuration. Therefore, we can exclude major configurational effects associated with the β_{CC} term; secondary effects could arise from the angular distortions in the second most stable conformational states and from the least stable ones.

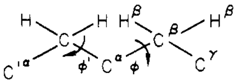
In order to test the validity of the above assumptions, we have calculated the chemical shifts of the central methylene carbon of HMTD, using eq 2, neglecting the β_{CC} term, and fitting the parameter γ to the experimental chemical shifts at 140 °C.

The results are shown in Table VII, where we report also the chemical shifts calculated with the three-state model and with Suter and Flory's model. All computations predict, in agreement with the experimental assignment and with the qualitative arguments illustrated earlier in this paper, that the tetrad spectrum is made of two overlapping triplets, the *r*-centered triplet being shifted at higher field with respect to the *m*-centered one.

The chemical shifts obtained with the present model are in excellent agreement with the experimental ones, except for the *mmm* peak, which is shifted upfield by 0.07 ppm. An even better agreement is found with Suter and Flory's model, again provided that eq 2 is applied with the same values of γ_i. The major defect of the three-state model is the exchange of the order of the resonances *mrr* and *mmm*; this error is reduced by using Tonelli's method (i.e., with Suter and Flory's model and shielding parameters according to ref 2), but the correct order is reached only by accounting for the angular distortions according to Figure 4.

Thus the calculations on the methylene carbon chemical shifts confirm the results obtained for the spectrum of the methyl carbon. However, we observe that the value of γ is much smaller for the methylene than for the methyl carbon, and that the difference between the two values is almost independent of the method of calculation. We cannot tell, at the moment, whether there is an intrinsic difference between the γ effects of the two types of carbon or if the reason lies in the simplification of the statistical methods[3,4] and/or in our estimates of the shielding parameters.

In the calculations presented above, we have assumed that the γ effect is a function of the dihedral angle CH_2–C^α–C^β–C^γ (ϕ) only, and we have used the same angular dependence of the CH_2 shielding parameter as that used for the methyl carbon, namely γ for G and G', 0 for T and G_+, and $-{}^1/_2\gamma$ for T_-. However, if the interpretation of the γ effect proposed by Beierbeck and Saunders[24] is correct, in the case of secondary and tertiary carbons the number of syn-axial β_{HC} interactions depends not only on the dihedral angle ϕ but also on the dihedral angle C'^α–CH_2–C^α–C^β (ϕ'). Considering first the nondistorted states T, G, and G' of the angles ϕ and ϕ', one finds that for any given value of ϕ the two more stable states of ϕ', T and G if C^α has configuration l, correspond to an equal number of β_{HC} interactions, while the removal of one such interaction is observed for the less stable stage G'. On the other hand, this state shows one β_{CC} contribution more than T and G, so that a net effect β_{CC}–β_{HC}, i.e., approximately ${}^1/_2\gamma$, should result when the dihedral angle ϕ' takes the conformation G'. As for the distorted conformations, inspection of the molecular models shows that, by analogy with the methyl case, a deshielding effect should be associated with the states T_- and G_+.



On the basis of these considerations, we repeated the calculations of the chemical shift for the central CH_2 of the HMTD stereoisomers, using the following expression:

$$\nu = \nu_0 + \sum_{i=1}^{5}(\gamma_i P_i + \gamma_i' P_i') \qquad (3)$$

where γ_i and P_i are defined as in eq 2, γ_i' is the shielding

Table VII
Experimental and Calculated Chemical Shifts (ppm) for the Methylene Carbon C_7 of 2,4,6,8,10,12-Hexamethyltridecane (HMTD)

		calcd			
				Suter-Flory model	
config	exptl[a]	this model	three-state model	following ref 2	using eq 2
rmr	45.634	45.654 (0.020)[b]	45.667	45.654	45.649
rrr	45.356	45.357 (0.001)	45.387	45.386	45.332
mmr	45.173	45.171 (−0.002)	45.138	45.147	45.189
mmm	44.812	44.741 (−0.071)	44.627	44.684	44.789
mrr	44.688	44.714 (0.026)	44.751	44.740	44.696
mrm	44.015	44.040 (0.025)	44.107	44.066	44.022
γ		−3.532	−3.655	−3.533	−3.952
MSE × 10^2		0.18	1.26	0.603	0.052

[a] For sample I at 140 °C in 1,2,4-trichlorobenzene, in ppm relative to internal reference HMDS. [b] Errors $\nu_{calcd} - \nu_{obsd}$ are given in parentheses.

parameter associated with the state *i* of the dihedral angle ϕ', and P_i' is the corresponding probability. The following values of γ_i' were tentatively used: $^1/_2\gamma$ for G', 0 for T and G, and $-^1/_2\gamma$ for T_- and G_+. The parameter γ was least-squares fitted as usual. The mean square error decreases from the previous value of 0.0018 to 0.0009 ppm,[2] the major changes occurring for the isomers *mmm* (shift of 0.08 ppm) and *rrr* (shift of −0.05 ppm); the value of γ is only slightly affected (−3.43 ppm). Of course, since only the less probable states are affected by the differences between eq 2 and 3, calculations on other systems are needed to prove that the above assignments of the γ_i' parameters are correct.

Conclusions

It has been shown how configurational effects on the CH_3 and CH_2 chemical shifts propagate along the polypropylene chain due to its cooperative nature: for this reason, even simplistic models are able to predict correct assignments of signals arising from distant substitutions. More caution has to be exerted when opposite effects balance each other, as in the case of the *mmm* and *mrr* CH_2 assignments.

The Boyd–Breitling[4] model of the polypropylene chain, as used in the present calculations, leads to theoretical CH_3 and CH_2 chemical shifts in good agreement with experiment and also reproduces thermodynamical data satisfactorily. Equally accurate results are obtained with the statistical model of Suter and Flory,[3] when the effects of angular distortions on the shielding are properly taken into account.

The best-fitting parameter γ for the methylene carbon is found to be considerably smaller than that for the methyl carbon. This result indicates that caution should be exerted when transferring such fitting parameters from one type of carbon to another.

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(27) The angular dependence of Figure 4, with a maximum around 120°, may also help to rationalize the chemical shift of the methyl carbon in other families of compounds. For example, the methyl carbon signal in 2-methylbicyclo[2.2.2]octane is 21.2 ppm relative to Me_4Si,[18] i.e., about 2 ppm upfield with respect to the equatorial methyls of methylcyclohexanes. Molecular energy calculations on this compound yield a minimum energy structure in which the methyl group is in a gauche arrangement (ϕ = 64°) with respect to C_4, while it forms dihedral angles of 133 and 171° with C_6 and C_7. It appears that the upfield shift due to the γ gauche interaction is partially balanced by the orientation of 133° with respect to C_6.
(28) For example, Stothers and co-workers report[16,17] syn-axial effects of 1.5 and 2.1 ppm, respectively, for the methyl carbons of 2,6-dimethylbicyclo[2.2.2]octane and the axial methyls of 3,3,5,5-tetramethylcyclohexanol. The minimum energy structures, calculated with the same method used for the TMCO analysis,[19,21] show distortions of the gauche dihedral angles from 64 to 76° in the first case and from 70 and 66 to 75 and 69° in the second one.
(29) For the sake of simplicity, in the text, now we shall use "methyl" for the methyl groups out of the chain plane, if we consider the compounds in the planar zigzag conformation.
(30) One of the reviewers, A. E. Tonelli, has pointed out that using the Suter–Flory RIS model[3] he was able to calculate the chemical shifts of $(CH_3)_9$ in the stereoisomers of HMHD in excellent agreement with the observed values[2] without inclusion of angle-dependent γ values. He pointed out also that the same results can be achieved for $(CH_2)_7$ of HMTD. We agree with him concerning $(CH_3)_9$ of HMTD (see Table V) and we are looking forward to the publication of his results concerning $(CH_2)_7$ of HMTD. Of course we will be quite happy if our experimental results can be of some use in improving the methods of calculation of ^{13}C chemical shifts of hydrocarbons.
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