low optical purity of the chains and could in principle be used for a quantitative evaluation. However an in-depth quantitative analysis requires completion of a detailed relaxation study.

Experimental Section

Polymerizations were performed at 50 °C for 3 days, using (*S*)- or (*RS*)-3-methyl-1-pentene (4 mL), $TiCl_3$ (3.2 mmol), $Al(CH_3)_3$ (1.7 mmol), and $Zn(CH_3)_2$ (1.4 mmol) in 7 mL of toluene. The yield of poly((*S*)-3M1P) and poly((*RS*)-3M1P) was 1.3 and 1.2 g, respectively.

Polymers were fractionated with boiling solvents as described in the literature.[8] The use of $Zn(CH_3)_2$—which is a fast transfer agent—resulted in regular benzene-soluble fractions. In fact, the solubility results from the low molecular weight of the fractions, rather than from the lack of stereoregularity.

A sample (0.6 g) of benzene-insoluble fraction of highly isotactic poly((*RS*)-3M1P) was thermally degraded under high vacuum about 500 °C, and the degradation products were collected in a trap at liquid nitrogen temperature.

^{13}C NMR spectra of highly isotactic diethyl ether insoluble, benzene-soluble fractions of poly((*RS*)-3M1P) and poly((*S*)-3M1P) were obtained at 140 °C on a Bruker HX-90 spectrometer operating at 22.63 MHz in the PFT mode. The pulse width was 3.6 μs (the pulse width for a 90° pulse is 15 μs). Dwell time of 200 μs was used with 16K of computer memory for the interferogram. Samples were prepared by dissolving the polymers in 1,2,4-trichlorobenzene and by adding 1% of hexamethyldisiloxane (HMDS) as an internal standard. The chemical shifts were converted to the Me_4Si scale.

^{13}C CP/MAS NMR spectra of benzene-insoluble fractions of poly((*RS*)-3M1P) and poly((*S*)-3M1P) and of thermally degraded poly((*RS*)-3M1P) were obtained on a Bruker CXP-300 spectrometer operating at 75.46 MHz, with magic angle rotation speed of 4.3 kHz. Free induction decays were generated by cross-polarization using a single contact pulse of 3 ms per ^1H spin locking and a recycle time of 5 s. The chemical shifts were referred to external Me_4Si.

Acknowledgment. Thanks are due to Dr. H. Forster (Bruker Analytische Messtechnik GMBH) for recording the ^{13}C CP/MAS NMR spectra and to Dr. D. R. Ferro for helpful discussion.

Registry No. Isotactic poly[(*S*)-3-methyl-1-pentene] (homopolymer), 28575-86-2; isotactic poly[(*RS*)-3-methyl-1-pentene] (homopolymer), 88611-18-1.

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Correlation between ^{13}C NMR Chemical Shifts and Conformation of Polymers. 4. Solid-State Spectra of Poly(3-methyl-1-pentene)

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ABSTRACT: A semiquantitative analysis of the solid-state ^{13}C NMR spectra of poly(3-methyl-1-pentene) is presented. The analysis is based on an empirical scheme for the computation of the chemical shifts of hydrocarbons, which takes into account conformational effects. The calculations provide a structural interpretation of the differences between the spectra of the optically active and the racemic polymers observed by Sacchi et al.[1] The effects of distortions of the helical structure from perfectly staggered conformations are also discussed.

The solid-state ^{13}C NMR spectra of racemic and optically active isotactic poly(3-methyl-1-pentene) ((poly(3M1P), shown schematically in Figure 1) have recently been studied by Sacchi et al.,[1] who also put forward an interpretation of the differences between the resonances observed for the two polymers in terms of the conformational structure of such polymeric chains.

In the present article we show a semiquantitative analysis of the ^{13}C chemical shifts observed by Sacchi et al.,[1] on the basis of an empirical scheme devised in this laboratory[2] for the computation of ^{13}C NMR chemical shifts of hydrocarbons.

Method of Calculation

The method applied here for computing the ^{13}C chemical shifts is a generalization of the well-known formula of Lindeman and Adams,[3] modified in order to account for conformational effects. According to our scheme, the chemical shift of a given carbon atom, characterized by a certain constitutional environment and by a certain average conformational state, can be computed as

$$\nu = \alpha_i + \sum_{j=2}^{4}\sum_{r} P'_{jr}\beta_{ij}(\phi'_r) + \sum_{j=2}^{4}\sum_{k=2}^{4}\sum_{r}\sum_{s} P_{jkrs}\gamma_{ijk}(\phi'_r,\phi_s) + (\delta \text{ effects} + ...) \quad (1)$$

where the parameters α_i, β_{ij}, and γ_{ijk} represent additive effects due to substituents in positions α, β, and γ, respectively, with respect to the observed atom C*. The index *i* is the number of carbons bonded to atom C*, the index *j* is the number of carbons bonded to an α carbon, and the index *k* is the number of carbons bonded to a β carbon. Finally the indexes *r* and *s* refer to the rotational states allowed for bonds C^*-C^α and $C^\alpha-C^\beta$, respectively.

The parameters β_{ij} and γ_{ijk} are conformation dependent. Thus the β contribution to the chemical shift of carbon

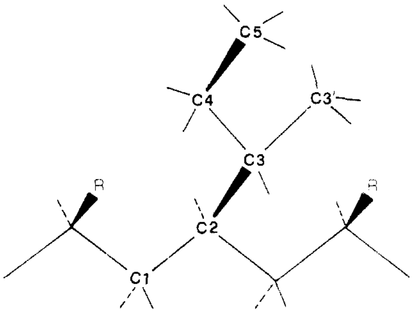
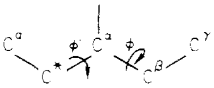


Figure 1. Schematic representation of the isotactic poly(3M1P) chain. For clarity, only one side chain, having configuration *S*, is shown in detail.

Table I
Parameters for the Computation of Primary, Secondary, and Tertiary ^{13}C NMR Chemical Shifts According to eq 2 and 3[a]

	primary	secondary	tertiary
α_i	5.70	15.16	23.15
β°_{i2}	9.82	10.01	6.99
β°_{i3}	19.38	16.98	13.14
γ°_{i2}	(0)	(0)	(0)
γ°_{i3}	−2.99	(−2.99)	−4.92
$\Delta\beta_{ij}(\mathrm{G})$[b]		(−2.71)	(−2.71)
$\Delta\gamma_{i2}(\mathrm{G})$	−4.62	(−4.62)	−5.97
$\Delta\gamma_{i3}(\mathrm{G})$	−7.34	(−7.34)	(0)

[a] Values in parentheses were kept fixed or assumed equal to another parameter in the least-squares fitting. [b] Both for $j = 2$ and $j = 3$, the value was taken equal to the difference between the two methine resonances observed for 2,3-dimethylbutane at low temperature.



C* arising from the atoms bonded to the atom C$^\alpha$ depends on the rotation angle ϕ' as well as on the number of carbons connected to C* and to C$^\alpha$. Similarly the γ contribution arising from the atoms bonded to C$^\beta$ is a function of the rotational angles ϕ' and ϕ. The coefficients P'_{jr} and P_{jkrs} represent respectively the probability of a β effect of type j in the conformational state ϕ'_r and the probability of a γ effect of type jk in the conformational state ϕ'_r, ϕ_s. Of course, such probabilities are normalized so that $\sum_r P'_{jr} = n_j$ (number of α carbons bonded to j carbons) and $\sum_r\sum_s P_{jkrs} = n_{jk}$ (number of β carbons bonded to k carbons and separated from the observed atom by a j-type α carbon). If we take as reference states of ϕ' and ϕ the conformations T, corresponding to the maximum number of trans (antiplanar) substituents on the opposite sides of the central bond, and we define $\beta^0_{ij} = \beta_{ij}(\mathrm{T})$ and $\gamma^0_{ijk} = \gamma_{ijk}(\mathrm{T,T})$, then we can rewrite eq 1 in the form

$$\nu = \nu_0 + \sum_j\sum_r{}' P'_{jr}\Delta\beta_{ij}(\phi'_r) + \sum_j\sum_k\sum_r{}'\sum_s{}' P_{jkrs}\Delta\gamma_{ijk}(\phi'_r,\phi_s) \qquad (2)$$

where the summations do not include the reference states and

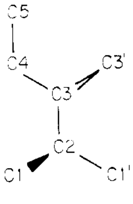
$$\nu_0 = \alpha_i + \sum_j n_j\beta^0_{ij} + \sum_j\sum_k n_{jk}\gamma^0_{ijk} \qquad (3)$$

is the chemical shift corresponding to the all-trans state.

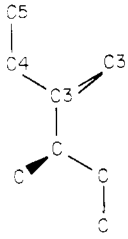
The parameters α_i, β^0_{ij}, γ^0_{ijk}, $\Delta\beta_{ij}$, and $\Delta\gamma_{ijk}$ utilized in the present work belong to a parameter set derived from the analysis[2] of the 59 hydrocarbons studied by Lindeman and Adams[3] and of a few other compounds. The complete set, apart from the parameters for quaternary carbons, which were fitted separately, contains 20 parameters, best fitted to 329 observations with a root mean square error of 0.50 ppm. The number of parameters was kept low, compared with the number of parameters which one could expect from the general equation (1), by making several simplifying assumptions to the conformation-dependent parameters. One of the assumptions was that the γ_{ijk} parameters are independent of the second index j; hence this index will be dropped hereafter. The values of the parameters utilized in the present paper are listed in Table I.

Model Compounds

The three compounds 2,3-dimethylpentane (I), *meso*-3,4-dimethylhexane (II), and *d,l*-3,4-dimethylhexane (III)



I



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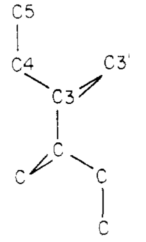


III

may be regarded as models of the poly(3-methyl-1-pentene) side chain. In order to make the reader familiar with our method, we show as an example the step-by-step calculation of the chemical shifts for the atoms of compound I.

(i) The reference state resonances ν_0 are readily obtained according to eq 3 upon inspection of the above structural formulas:

$$\nu_0(\mathrm{C1}) = \nu_0(\mathrm{C1'}) = \alpha_1 + \beta^0_{13} + \gamma^0_{13} = 22.09$$

$$\nu_0(\mathrm{C2}) = \alpha_3 + \beta^0_{33} + \gamma^0_{32} = 36.29$$

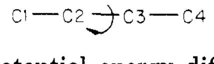
$$\nu_0(\mathrm{C3}) = \alpha_3 + \beta^0_{33} + \beta^0_{32} = 43.28$$

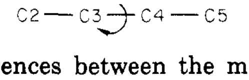
$$\nu_0(\mathrm{C4}) = \alpha_2 + \beta^0_{23} + \gamma^0_{23} = 29.15$$

$$\nu_0(\mathrm{C3'}) = \alpha_1 + \beta^0_{13} + \gamma^0_{13} + \gamma^0_{12} = 22.09$$

$$\nu_0(\mathrm{C5}) = \alpha_1 + \beta^0_{12} + \gamma^0_{13} = 12.53$$

(ii) Then the usual methods of molecular mechanics are utilized for calculating the conformer populations in the frame of the rotational isomeric state approximation. The populations were determined on the basis of the differences between the various potential energy minima, obtained by means of a minimization procedure in Cartesian coordinates, without any geometrical restraint. We had to use this approximation, which does not account for differences in the shape of the potential energy wells, due to the large number of compounds treated in our study.[2] Compound I has two conformational degrees of freedom, which we represent by means of the two dihedral angles χ_1 and χ_2.





The potential energy differences between the minima corresponding to the various conformers, computed utilizing the force field of Warshel and Lifson,[4] are shown in Table II, together with the room-temperature Boltzmann populations.

(iii) By properly adding up the conformer populations, one can calculate the probability coefficients P' and P of eq 2 and obtain the conformational averages for the chemical shifts of the various atoms. Considering first the methyl carbons, we note that the diastereotopic atoms C1

Table II
Relative Potential Energies for the Conformers of 2,3-Dimethylpentane

conformer[a] χ_1, χ_2	ΔE, kcal/mol	population $p(\chi_1, \chi_2)$
T, T	0.13	0.222
T, G	0	0.279
T, $\bar{\text{G}}$[b]	2.31	0.003
G, T	0	0.278
G, G[b]	1.85	0.006
G, $\bar{\text{G}}$[b]	2.61	0.002
$\bar{\text{G}}$, T	0.70	0.084
$\bar{\text{G}}$, G[b]	1.70	0.008
$\bar{\text{G}}$, $\bar{\text{G}}$	0.51	0.118

[a] Conformation T (trans-planar) corresponds to $\chi \simeq 180°$, G indicates the positive (clockwise) gauche conformation ($\chi \simeq 60°$), and $\bar{\text{G}}$ is the counterclockwise gauche conformation ($\chi \simeq -60°$). [b] These high-energy minima, all showing one δ syn-axial interaction, actually correspond to somewhat distorted conformations. Their statistical weights were halved in order to account approximately for the narrowness of the potential wells. Slight effects arising from the angular distortions in these conformers were accounted for in the application of eq 2.[2]

and C1′ are only involved in one γ interaction, which is a function of the rotation angle about the C2–C3 bond. Hence for these atoms eq 2 simply yields

$$\nu(\text{C1}) = \nu_0(\text{C1}) + p_1(\text{G})\Delta\gamma_{13}(\text{G}) = 22.09 - 0.285(7.34) = 20.00$$

$$\nu(\text{C1}') = \nu_0(\text{C1}') + p_1(\text{T})\Delta\gamma_{13}(\text{G}) = 22.09 - 0.503(7.34) = 18.40$$

where $p_1(\text{G})$ and $p_1(\text{T})$ are the probabilities that χ_1 takes the conformations G and T, corresponding respectively for C1 and C1′ to one extra γ-gauche interaction with respect to the reference state. Analogously one calculates

$$\nu(\text{C5}) = \nu_0(\text{C5}) + p_2(\bar{\text{G}})\Delta\gamma_{13}(\text{G}) = 12.53 - 0.122(7.34) = 11.63$$

$$\nu(\text{C3}') = \nu_0(\text{C3}') + p_1(\text{T})\Delta\gamma_{13}(\text{G}) + (p_2(\text{T}) + p_2(\bar{\text{G}}))\Delta\gamma_{12}(\text{G}) = 22.09 - 0.503(7.34) - 0.703(4.62) = 15.15$$

The tertiary carbon C3 shows only β conformational effects, arising from the all-gauche conformations of χ_1 (T and G) and χ_2 ($\bar{\text{G}}$)

$$\nu(\text{C3}) = \nu_0(\text{C3}) + (p_1(\text{T}) + p_1(\text{G}))\Delta\beta_{33}(\text{G}) + p_2(\bar{\text{G}})\Delta\beta_{32}(\text{G}) = 43.28 - 0.790(2.71) - 0.122(2.71) = 40.81$$

Finally, the tertiary carbon C2 and the secondary carbon C4 show both β and γ conformational effects. The latter ones in such cases depend on both dihedral angles χ_1 and χ_2, and application of eq 2 leads to the following results:

$$\nu(\text{C2}) = \nu_0(\text{C2}) + (p_1(\text{T}) + p_1(\text{G}))\Delta\beta_{33}(\text{G}) + (p(\text{TG}) + p(\bar{\text{G}}\bar{\text{G}}))\Delta\gamma_{32}(\text{G}) = 36.29 - 0.790(2.71) - 0.397(5.97) = 31.78$$

$$\nu(\text{C4}) = \nu_0(\text{C4}) + p_2(\bar{\text{G}})\Delta\beta_{23}(\text{G}) + p(\text{GT})\Delta\gamma_{23}(\text{G}) - (p(\bar{\text{G}}\text{G}) + p(\text{T}\bar{\text{G}}))\gamma^0{}_{23} = 29.15 - 0.122(2.71) - 0.278(7.34) + 0.011(2.99) = 26.81$$

A simpler treatment assuming the dependence of $\nu(\text{C2})$ on χ_2 and $\nu(\text{C4})$ on χ_1 would differ from the present calculation with regard to the high-energy conformers showing a δ syn-axial interaction. The details concerning such small effects, which are irrelevant to the main purpose of this article, will be found in ref 2.

The chemical shifts calculated for the three model compounds are indicative of the accuracy obtainable with the method adopted here. The results are shown in Table III, where for comparison we also list the chemical shifts computed according to Lindeman and Adams[3] and to Beierbeck and Saunders.[5] We point out that the stereochemical differences between resonances of constitutionally equivalent carbons are much better reproduced by the present method than in previous work;[5] however, the stereochemical shifts of methyl carbons are still significantly underestimated.

Results and Discussion

The crystal structure of poly((*S*)-3M1P) was determined by Petraccone et al.,[6] who found a helical conformation with four monomer units per turn. In this structure the side-chain conformation is characterized by two equiprobable states (T and G) for the rotation angle C2–C3–C4–C5. These findings were further supported by conformational energy calculations performed by the same group,[7] according to which the fourfold left-handed helix of poly((*S*)-3M1P) is favored with respect to the nearly equienergetic right-handed fourfold helix by the possibility of having two side-chain conformations. These calculations show also that isolated threefold helices have energy comparable with that of the fourfold ones. The crystal structure of poly((*RS*)-3M1P) differs from that of the optically active polymer[8,9] but has not been determined. According to Pino et al.[10] the *R* and *S* *sec*-butyl side chains are isomorphous to a large extent. This hypothesis seems to be consistent with the results of energy calculations.[7] It has been shown by Zambelli et al.[8] that poly((*RS*)-3M1P) is a mixture of copolymer chains containing prevailingly either the *R* or the *S* monomer, with a ratio of about 2.5:1 between the two monomer species. In light of all these facts we can attempt to compute the chemical shifts of crystalline poly((*S*)-3M1P) and poly((*RS*)-3M1P), assuming that a single chain of the latter (e.g., one with prevailing *S* units) is in an idealized (left-handed) helical conformation where units *R* and *S* have exchanged positions of C4 and C3′ and where the more common *S* units can present two conformations (T and G) of the side chain

Table III
Comparison between Observed and Calculated ^{13}C Chemical Shifts of Model Compounds I-III

	I				II				III			
		calcd				calcd				calcd		
atom	exptl ref 3	this work	ref 5	ref 3	exptl ref 3	this work	ref 5	ref 3	exptl ref 3	this work	ref 5	ref 3
C5	11.6	11.63	11.7	11.36	11.8	11.99	11.7	11.36	11.8	12.04	11.7	11.36
C3′	14.5	15.15	16.2	15.66	15.8	15.35	17.2	16.15	13.8	14.27	16.4	16.15
C4	26.8	26.81	27.7	26.66	25.8	25.83	28.1	26.91	27.6	27.58	28.2	26.91
C3	40.6	40.81	39.2	41.20	39.5	38.86	38.7	39.13	38.5	38.05	38.7	39.13
C2	31.9	31.78	32.9	32.53								
C1	20.0	20.00	19.5	19.14								
C1′	17.7	18.40	18.8	19.14								

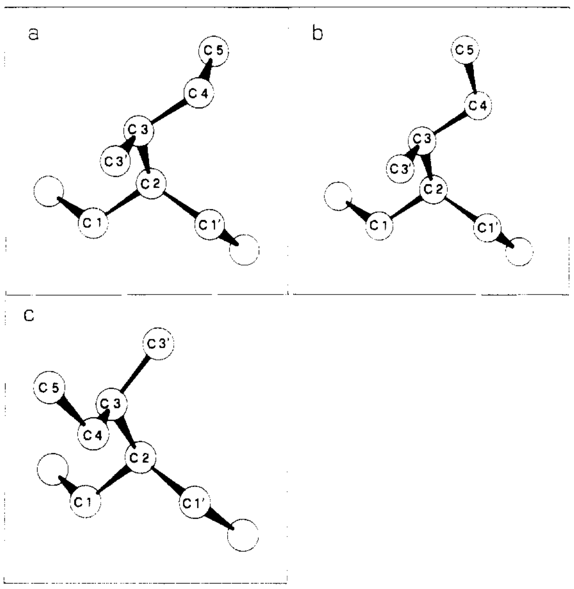


Figure 2. The three side-chain conformations (χ_1, χ_2) allowed for a left-handed helical chain of poly((*RS*)-3M1P): (a) unit *S*, conformation TG; (b) unit *S*, conformation TT; (c) unit *R*, conformation GT. In all cases the rotation angles about the backbone bonds C1–C2 and C2–C1′ are those for the left-handed helix (−149° and 81°, respectively[6]).

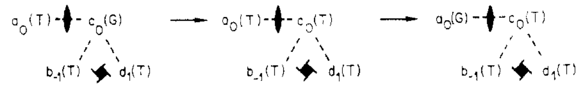
terminal, while the less common *R* units have the side chain confined in the only allowed conformation (T). A complete description of the side-chain conformation in the three cases is given in Figure 2; the conformation is defined as for model compound I through the dihedral angles χ_1 and χ_2.

The chemical shifts of the various carbon atoms of a left-handed helix are given according to eq 1 by the following expressions:

$$\begin{aligned}
\nu(\mathrm{C5}) &= \alpha_1 + \beta^0{}_{12} + \gamma^0{}_{13} \\
\nu_S(\mathrm{C3'}) &= \alpha_1 + \beta^0{}_{13} + \gamma^0{}_{13} + \Delta\gamma_{13}(\mathrm{G}) + p_2(\mathrm{T})\,\Delta\gamma_{12}(\mathrm{G}) \\
\nu_R(\mathrm{C3'}) &= \alpha_1 + \beta^0{}_{13} + \gamma^0{}_{13} + \Delta\gamma_{13}(\mathrm{G}) \\
\nu_S(\mathrm{C4}) &= \alpha_2 + \beta^0{}_{23} + \gamma^0{}_{23} \\
\nu_R(\mathrm{C4}) &= \alpha_2 + \beta^0{}_{23} + \gamma^0{}_{23} + \Delta\gamma_{23}(\mathrm{G}) \\
\nu(\mathrm{C3}) &= \alpha_3 + \beta^0{}_{32} + \Delta\beta_{32}(\mathrm{G}) + \Delta\gamma_{32}(\mathrm{G}) \\
\nu_S(\mathrm{C2}) &= \alpha_3 + \beta^0{}_{33} + 2\,\beta^0{}_{32} + \Delta\beta_{33}(\mathrm{G}) + 2\,\gamma^0{}_{33} + (1 - p_2(\mathrm{T}))\Delta\gamma_{32}(\mathrm{G}) \\
\nu_R(\mathrm{C2}) &= \alpha_3 + \beta^0{}_{33} + 2\,\beta^0{}_{32} + \Delta\beta_{33}(\mathrm{G}) + 2\gamma^0{}_{33} \\
\nu(\mathrm{C1}) &= \alpha_2 + 2\,\beta^0{}_{23} + 2\,\gamma^0{}_{23} + \Delta\gamma_{23}(\mathrm{G}) + \Delta\gamma_{22}(\mathrm{G}) \qquad (4)
\end{aligned}$$

Here $p_2(\mathrm{T})$ represents the probability that the dihedral angle χ_2 is in the trans state: following Petraccone et al.,[6] we take $p_2(\mathrm{T}) = 0.5$. The assumption underlying the above expression of $\nu_S(\mathrm{C2})$ and $\nu_S(\mathrm{C3'})$ is that the two conformations T and G are in rapid equilibrium on the NMR time scale. This assumption, which is necessary for justifying at the same time the X-ray analysis[6] and the observation of single C2 and C3′ resonances,[1] requires clarification. In fact, according to Petraccone et al.,[6] the statistical distribution of the two conformations cannot be completely random, owing to strong repulsive interactions between two side-chains G related by a pseudotwofold axis and to less severe interactions between successions of T side chains related by a pseudofourfold screw axis.

We briefly report the results of energy calculations performed in this laboratory[11] with the purpose of estimating the barrier hindering the rotation about the C3–C4 bond in the solid state. We first optimized the hydrogen coordinates of an isolated helical chain, for both conformations T and G, utlizing the experimental positions of the carbon atoms.[6] Then these coordinates were used to generate a fragment of the crystal of poly((*S*)-3M1P), setting the side chains in orderly alternated T and G conformations, so as to avoid the forementioned intermolecular repulsive contacts. The fragment contains 141 atoms and is formed by four side chains, which were treated as movable except for the C2 atom, and by the surrounding atoms appreciably interacting with the movable part, which were kept fixed and acted as a constraint to the movement of the four side chains. One of these, c_0, is related to a_0 by the pseudotwofold axis and to b_{-1} and d_1 by the screw axis. The state A of this system, after minimization of the total energy with respect to the coordinates of the 4 × 12 movable atoms, represents a model of one of the two ordered lowest energy states of the crystal. By using the two χ_2 dihedral angles of c_0 and a_0 as reaction coordinates, we calculated the energy cost for flipping the conformation of a couple of side chains, following the scheme:



($E = 0$) ($E = 1.8$ kcal/mol) ($E = 2.1$ kcal/mol)

A B C

The two minima A and B are separated by a saddle point with $E = 2.5$ kcal/mol for $\chi_2 = 120°$, and a similar barrier is found between B and C (saddle point with $E = 4.25$ kcal/mol); the height of these barriers is practically the same as for the χ_2 rotation in isolated 2,3-dimethylpentane. The instability of B and C arises from the unfavorable T···T contacts (about 1 kcal/mol per contact) between the side chains related by the screw axis; by rotating the side chains b_{-1} and d_1, again through similar barriers, the defect can be transferred to other side chains, leaving the fragment under inspection in the ground state alternative to state A. As such a concerted flipping requires to overpass a total energy barrier on the order of 5 kcal/mol, we can qualitatively conclude that at room temperature the exchange of the C5 positions in crystalline poly((*S*)-3M1P) is likely to be fast on the NMR time scale.[12]

The values of the chemical shifts computed by utilizing expressions 4 and the parameter set of Table I are listed in Table IV, together with the values observed by Sacchi et al.[1] and the values predicted according to the formula of Lindeman and Adams.[3] We first point out that according to expressions 4, only three of the six chemical shifts of a unit *R* should differ from the corresponding values of a unit *S*. Thus, under our hypothesis, the spectrum of solid poly((*RS*)-3M1P) should present, besides the same six resonances of poly((*S*)-3M1P), three secondary peaks arising from atoms C3′, C4, and C2 of the less probable type of unit in a given chain. This result justifies the assignment by Sacchi et al.[1] of the three resonances given in the last column of Table IV. The three stereochemical shifts $\nu_R - \nu_S$ are rather large (4.2, −6.1, and 3.9 ppm respectively for C3′, C4, and C2); the agreement of the calculated values (5.0, −7.3, and 3.0 ppm) is reasonably good, considering the large size of the effects involved. We note that the hypothesis of a single χ_2 conformation in poly((*S*)-3M1P) would lead to calculated $\nu_R - \nu_S$ differences for C3′ and C2 equal to 7.3 and 0.0 ppm (for $p_2(\mathrm{T}) = 1$) or equal to 2.7 and 6.0 ppm (for $p_2(\mathrm{T}) = 0$); the disagreement with the observed differences lends further

Table IV
Comparison between Observed and Calculated ^{13}C Chemical Shifts[a] of Poly((*RS*)-3M1P)

<table>
<tr><th></th><th colspan="3">calcd</th><th colspan="2"></th></tr>
<tr><th></th><th></th><th colspan="2">this work</th><th colspan="2">obsd (ref 1)[b]</th></tr>
<tr><th>atom</th><th>ref 3</th><th>S</th><th>R</th><th>S</th><th>R</th></tr>
<tr><td>C5</td><td>11.36</td><td colspan="2">12.53</td><td colspan="2">13.7 (14.1)</td></tr>
<tr><td>C3′</td><td>16.64</td><td>12.44</td><td>17.47</td><td>13.7 (14.1)</td><td>17.9</td></tr>
<tr><td>C4</td><td>27.16</td><td>29.15</td><td>21.81</td><td>28.9 (29.0)</td><td>22.8</td></tr>
<tr><td>C1</td><td>34.10</td><td colspan="2">31.18</td><td colspan="2">32.4</td></tr>
<tr><td>C3</td><td>37.06</td><td colspan="2">34.60</td><td colspan="2">36.7</td></tr>
<tr><td>C2</td><td>37.45</td><td>34.74</td><td>37.72</td><td>36.7 (38.0)</td><td>40.6</td></tr>
</table>

[a] Referred to $\mathrm{Me_4Si}$. [b] Values in parentheses refer to poly((*S*)-3M1P).

support to the hypothesis of two conformations in rapid equilibrium.

A second important point concerns the discrepancies between each observed and calculated chemical shift. Inspection of Table IV shows an average difference of +1.4 ppm; this large deviation can be ascribed to either or both of the following causes: (a) deviation from staggered conformations and (b) specific solid-state effects. Conformational deformations may markedly affect the chemical shifts, at least for some atoms. In fact expressions 4 were derived for a perfectly all-staggered structure (corresponding to the threefold helix), while the fourfold helix observed for poly((*S*)-3M1P) shows deformations as large as 30°; according to Corradini and co-workers,[6] the experimental values for a pair of adjacent main-chain dihedral angles are −149° and 81°, while the values calculated by them for the energy minima[7] are −155° and 78°. The effects of these torsional deformations, which should affect the chemical shifts of atoms C1, C2, and C3, are perhaps even smaller than one would expect. Indeed (assuming that all the discrepancies of Table IV arise only from the deformations) these three atoms would retain about 70% of the upfield shifts due to γ-gauche interactions. On the other hand, such shifts were completely neglected for deformations only slightly larger, due to δ syn-axial interactions, in studies[13-15] which successfully interpreted the spectra of polypropylene in solution.

Smaller deformations of the rotation angle around bond C1–C2 may also affect the chemical shifts of atoms C3′ and C4 (and again C2). On the contrary, no distortion effects can be invoked to explain the discrepancy of the calculated chemical shift of the methyl carbon C5 with respect to the values observed in the crystalline polymers, since energy calculations indicate two normal trans and gauche states for the rotation angle χ_2. It is interesting to compare the C5 resonance of poly(3M1P) with those of the model compounds I–III of Table III, which are well reproduced by the calculations. The calculated ν(C5) is lower in I with respect to the polymer, due to the upfield shift associated with the all-gauche conformer ($\bar{G}$) present in I in nonnegligible amounts (~10%). The small relative downfield shift observed in II reflects the decrease of the all-gauche conformer population when a methyl group is added on the other side of the chain. Such a difference is exaggerated by our calculation, and thus a large underestimate of the effect of the complete disappearance of the conformer is unlikely. We point out that the population of the all-gauche conformer in poly(3M1P) must be negligible also in solution, as it is necessarily associated with δ syn-axial interactions, and indeed the calculated ν(C5) is in reasonable agreement with the value of 12.8 ppm observed in solution.[1] The downfield shift in the crystalline polymers must then arise from specific solid-state effects. This situation resembles that of the methyl resonance of crystalline isotactic polypropylene, which has been observed by Bunn et al.[16] to be shifted by 1.5 ppm upfield with respect to the syndiotactic resonance; also in that case the difference cannot be explained in terms of changes in the conformational structure.

We finally note that our calculations do not explain the difference of 1.3 ppm observed by Sacchi et al.[1] between the crystalline poly((*S*)-3M1P) and poly((*RS*)-3M1P) methine resonances assigned as ν(C2); in fact, a conformational change, such as a shift of the poly((*RS*)-3M1P) chain toward the threefold helix, should probably involve changes in more than one atom. On the other hand a decrease of p_2(T) (population of the trans state of the side-chain end) should have opposite effects on ν(C2) and ν(C3′).

In conclusion, our computational scheme offers a rather crude representation of the poly(3M1P) spectra; however, unlike more simplistic methods, it is able to explain semiquantitatively some of the features observed by Sacchi et al.[1]

In the above calculations we have assumed that the poly((*RS*)-3M1P) chain has an idealized helical structure. Sacchi et al.[1] found essentially the same spectrum for the amorphous solid and also very close chemical shifts in solution, where the chain structure should mainly consist of left- and right-handed helical segments.[7,17-19] In this case the intensity of the secondary resonances (ν_R in Table IV) corresponds to the sum of the concentrations of units *R* in the left-handed helix (P_{Rl}) and of units *S* in the right-handed one (P_{Sr}). While energy calculations are being carried on in this laboratory, to obtain a detailed statistical treatment of the poly((*RS*)-3M1P) chain, here we mention a result obtained with a simple two-parameter model. The parameters are the statistical weight of a unit *R* in the left-handed helix (taken near 0.5 following Corradini and co-workers[6,7]) and the average energy for a helix inversion. Taking various values of the parameters, with a ratio of 70 to 30 between the concentrations of the two monomeric species and with a nearly Bernoullian distribution, the result is that the sum $P_{Rl} + P_{Sr}$ always nearly equals the concentration of the less common species. Therefore the relative intensity of the secondary peaks should still represent a measure of the proportion of units *R* and *S* in a copolymer chain.

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Registry No. I, 565-59-3; II, 52949-33-4; III, 52919-17-2; isotactic poly((*RS*)-3M1P), 88611-18-1.

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Aggregation of Ion Pairs in Sodium Poly(styrenesulfonate) Ionomers: Theory and Experiment

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ABSTRACT: Theory of the effect of ion-pair clustering on chain dimensions was compared with mean-square radii of gyration determined on poly(styrenesulfonic acid) ionomers by small-angle neutron scattering (SANS). Reasonable agreement between theory and experiment was obtained by setting the surface energy of cluster formation (the only arbitrary parameter) equal to 8.9 kcal/mol of ion pairs. Since theory predicted more ion pairs per cluster than could be accommodated in spherical clusters, lamellar cluster formation was assumed. Theory predicted about 15 and 12 ion pairs per cluster for polymer containing 1.9 and 8.5 mol % ionic repeat units, respectively. The data suggest, however, that the clusters themselves may aggregate to form higher order structures for ionic concentrations greater than about 5–6 mol %. The theory was also compared with results from SANS chain dimension measurements on the acid precursor of the 1.9 mol% ionomer. Predictions of chain extension due to carboxyl–carboxyl hydrogen bonding were in good agreement with the reported value for the polymer if about 50% of the carboxyl groups participate in hydrogen bonding. The reported mean-square radius of gyration was not, however, known to sufficient accuracy to offer a critical test of the theory.

Introduction

An overwhelming body of experimental evidence indicates that there is aggregation of ion pairs in ionomers.[1] In spite of all of this evidence, however, there is still no clear picture of the nature of the aggregates. In this paper we suggest that measurements of chain dimensions by small-angle neutron scattering (SANS) interpreted in terms of recent theory will lend further insight to the nature of ionomer structure. The arguments will be illustrated by results from recent measurements of neutron scattering from a set of sodium poly(styrenesulfonate) ionomers prepared from polystyrene of 1.0×10^5 molecular weight.[2] Ion content varied from 1.9 to 8.5 mol %. Results were also reported for scattering experiments on a 1.9 mol % unneutralized acid sample. Polymer preparation and characterization and the scattering experiments are described in detail in a previous paper.[2]

Results of the neutron scattering experiments were incontrovertible; the z-average radius of gyration of the polymer molecules increased monotonically with increasing ion content. Although qualitative arguments were given associating this phenomenon with ion-pair association,[2] more detailed interpretation requires a theory framed in terms of molecular parameters that are, at least in principle, determinable from independent experiments. One of us recently published such a theory[3] based on the statistical mechanics of chain-like molecules and energy considerations of ionic interactions introduced by Eisenberg.[4] Statistical considerations alone indicate that clustering of ion pairs should indeed result in extension of the chain-like molecules, and a simple model (to be described later) gives a simple closed-form expression for chain extension as a function of the fraction of repeat units participating in cluster formation, the number of repeat units in each cluster, polymer concentration, and the statistics of the unperturbed polymer chains. By extending the theory to include entropy effects and a simple model for energy of cluster formation, the analysis gives a prediction of chain extension and number of repeat units per cluster as a function of one arbitrary parameter—the change in surface energy of a cluster associated with the addition of one repeat unit.

The theory was formulated for an assembly of monodisperse chains. Since the heterodispersity indices of the polymers used in the experiments were 1.05–1.06, it is reasonable to assume that any serious disagreement be-

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