This effect is consistent with the observation (see Figure 11) that bonds in the main chain which are one bond away from the branch point have an enhanced a priori probability of being in the trans conformation. The value of $p_{t;i}$ is 0.733 for these bonds in the main chain, and 0.740 is obtained for the second bond in the n-butyl groups.

$$\begin{bmatrix} 0.356 & 0.192 & 0.192 \\ 0.082 & 0.044 & 0.004 \\ 0.082 & 0.004 & 0.044 \end{bmatrix} \tag{49}$$

$$\begin{bmatrix} 0.291 & 0.157 & 0.157 \\ 0.124 & 0.067 & 0.006 \\ 0.124 & 0.006 & 0.067 \end{bmatrix} \tag{50}$$

The results corresponding to (49) for the cases where $n_2 = 2$ are shown in (51) and (52). Both n-butyl branches in the racemic (dl) pair, as well as branch 5 in the meso (ll) pair, yield the $p_{\xi\eta;i}$ shown in (51), while (52) is obtained for ${}_3p_{\xi\eta;3}$ with the meso (ll) pair. Comparison with (49) reveals that the conformation of an n-butyl group is only slightly affected by another n-butyl group even when $n_2 = 2$. This result indicates that the conformations of the side chain in a vinyl polymer containing n-butyl groups would be essentially independent of one another.

$$\begin{bmatrix} 0.360 & 0.194 & 0.194 \\ 0.075 & 0.040 & 0.004 \\ 0.084 & 0.004 & 0.045 \end{bmatrix} \tag{51}$$

$$\begin{bmatrix} 0.360 & 0.194 & 0.194 \\ 0.084 & 0.045 & 0.004 \\ 0.075 & 0.004 & 0.040 \end{bmatrix} \tag{52}$$

A previous attempt[18] to treat branched polyethylene in the rotational isomeric state approximation differs significantly from the present work. A distinction of utmost importance resides in the configuration partition function used. The present work utilizes the exact configuration partition function for the entire branched molecule. In contrast, Tonelli[18] does not write a configuration partition function for the molecule, but instead writes approximate expressions for individual linear chains within the branched polyethylene. Consequently his treatment is not capable of evaluating the effect of branching on conformational properties with the rigor available in the rotational isomeric state theory. A further important distinction is that certain of the statistical weight matrices used by Tonelli[18] were formulated improperly. Specifically, his $\mathbf{U}_{i-2}$ and $\mathbf{U}_{i+2}$ (our ${}_1\mathbf{U}_{n_1-1}$ and ${}_2\mathbf{U}_3$) are in error; they should be formulated as (1), since the rotations represented by ${}_1\phi_{n_1-1}$ and ${}_2\phi_3$ bring about three- and four-bond interactions identical with those which occur in the linear molecule. Furthermore, the statistical weight matrix which he writes as $\mathbf{U}_i$ is appropriate *only* when ${}_3\phi_1$ is restricted to the reference conformation. Nevertheless, Tonelli's qualitative conclusions that bonds involving ${}_1\mathrm{A}_{n_1}$ have a reduced a priori probability of being in the trans state, and the next bond away from the branch point has an enhanced a priori probability of being in the trans state, are in agreement with the quantitative results obtained in the present work.

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Mean Dimension of a Polymer Chain in Athermal Solutions and in Bulk Phase

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ABSTRACT: Athermal polymer solutions are approximated by an assembly of nonintersecting self-avoiding walks on the simple cubic lattice. The mean-square end-to-end distance $\langle r_n^2 \rangle$ of walks involving n lattice sites is evaluated for n = 6, 10, 20, and 30 by means of a Monte Carlo method allowing for handling of highly concentrated systems; the fractional occupancy φ of the lattice approaches 0.95 in some cases. It is observed that $\langle r_n^2 \rangle$ diminishes steadily as φ increases. The relative decrease of $\langle r_n^2 \rangle$ with respect to the mean-square distance $\langle r_n^2 \rangle_0$ of the infinitely diluted system grows with n. Extrapolating the data to $\varphi = 1$(bulk polymer), we find that $\langle r_n^2 \rangle_1$ varies approximately like $n^{1.08}$ in the asymptotic limit (to be compared with $\langle r_n^2 \rangle_0 \sim n^{1.20}$). This result is compared with existing theories and presently available experimental data.

The configuration of polymer chains in solution is determined by both intra- and intermolecular forces. In the *athermal* case both of these forces reduce to exclusion effects and are expected to act in opposite directions if one takes the random flight chain as reference state. On the one hand, intra-exclusions eliminate self-intersecting configurations of the chain, increasing thereby its average spatial extension; on the other hand, the presence of other polymer molecules in the neighborhood is likely to hamper extended configurations preferentially, leading to a decrease of the mean dimensions of the chain. In what follows we use the mean-square end-to-end distance $\langle r^2 \rangle$ to characterize the average chain extension in space, as this quantity is the easiest one to compute either theoretically or numerically. (The mean-square radius of gyration is likely to be more appropriate but it requires much more work.)

As far as the case of an isolated chain is concerned, with purely repulsive interactions between its n segments, the following asymptotic form

$$\langle r_n^2 \rangle \sim n^{1.20} \tag{1}$$

seems fairly well established as mean field theories,[1,2] exact enumerations on lattices,[3] and recent Monte Carlo simulations[4] all agree with it. Few theoretical results are available for the variation of $\langle r_n^2 \rangle$ with polymer concentration. Bluestone and Vold got some numerical evidence that $\langle r_n^2 \rangle$ is decreased by the neighborhood of another chain[5] and this was recently confirmed by Curro for n-alkanes.[6] In a previous paper we sampled $\langle r_n^2 \rangle$ for assemblies of chains of various lengths (n = 6, 10, 20, and 30) on the simple cubic lattice, for a large range of concentrations;[7,8] a neat decrease of $\langle r_n^2 \rangle$ was observed as the polymer volume fraction φ increases and the following asymptotic form was derived for low values of φ

$$\langle r_n^2 \rangle_\varphi / \langle r_n^2 \rangle_0 \simeq 1 - 0.043 n^{0.72} \varphi \tag{2}$$

where $\langle r_n^2 \rangle_0$ corresponds to infinite dilution. Not much could be said, however, about highly concentrated systems as data were lacking especially for chains of 20 and 30 segments, so that we did not try at that time to extrapolate the available results to the case of bulk polymer ($\varphi = 1$).

The major difficulty we met for highly concentrated systems was the extreme slowness of the Monte Carlo technique generating successive configurations. We recently replaced it by a more efficient *shuffling* of the assembly, combined with an original coding system, so that we are now able to report additional data at high concentrations, allowing reasonable extrapolations to the bulk case.

Description of the Model and Method

We simulated athermal polymer solutions by considering assemblies of nonintersecting chains, each of which occupies n sites of a simple cubic lattice. Each chain corresponds to a five-choice self-avoiding walk of $n - 1$ steps (i.e., bond angles of both 90 and 180° are permitted). A long sequence of configurations is generated by a Monte Carlo technique from which $\langle r^2 \rangle$ is deduced. Chain lengths n = 10, 20, and 30 were considered for fractional occupancies of the lattice extending as high as 0.95, 0.90, and 0.70, respectively. For all systems studied the total number N of chains ranges between 100 and 765, while the number of analyzed configurations lies between 10^3 and 10^4.

The Monte Carlo technique used as low φ values for generating sequential configurations was described in our previous paper.[8] In short, each chain is successively scrutinized from its first to last segment and various kinds of moves of individual segments are tried by gambling; a move is accepted *if it is not prohibited* by the presence of segments belonging to the same or to other chains. This method becomes however almost impracticable at high density. In this region a much better way to generate sequential configurations is to view chain movements as rearrangements of empty sites on the lattice. Accordingly a new technique was developed where essentially one selects an empty site at random and one looks if a neighboring polymer segment can possibly be transferred to it. The actual procedure may be summarized as follows.

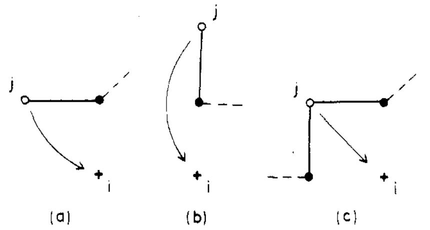

Figure 1. Rearrangements of empty sites on the lattice, by moving a T or I segment from site j to site i.

To each lattice site we associate a code number which stores the following information: (a) state of the site (occupied by a polymer segment or empty); (b) if occupied, the nature of this segment (terminal or internal segment, T or I segment); (c) for a T segment, the relative position of the adjacent segment; (d) for an I segment, the relative positions of the two adjacent segments.

Starting from a given configuration of the chains on the lattice, we then proceed as follows: (a) an empty site i is selected at random; (b) another site j is randomly selected among the second (12) and fourth (6) neighbors of i; (c) if j is either a second or a fourth neighbor of i occupied by a T segment, with its adjacent segment located on a first neighbor of i, the T segment is transferred on site i (see Figures 1a and 1b); (d) if j is a second neighbor of i occupied by an I segment, with both its two adjacent segments located on first neighbors of i, the I segment is moved to site i (see Figure 1c).

This process is repeated until at least half of the segments of the whole system have been moved; the value of $\langle r^2 \rangle$ is computed for the newly built configuration and the rearrangement process of empty sites is then restarted. The time saving of the method is extremely important; indeed we know whether a move is possible or not just by looking at the one code number relative to the selected site j. Moreover the efficiency of the method increases with the density because the probability for finding a transferable segment increases.

Table I
Values of $\langle r^2 \rangle$ for Various n-Mer Assemblies[a]

$n = 10$		$n = 20$		$n = 30$	
φ	$\langle r^2 \rangle_\varphi$	φ	$\langle z^2 \rangle_\varphi$	φ	$\langle z^2 \rangle_\varphi$
0	14.781[b]	0	36.32 ± 0.03[8]	0	60.40 ± 0.05[c]
0.7983 (328)	13.122 ± 0.090	0.5957 (123)	31.06 ± 0.32	0.4999 (546)	48.81 ± 0.32
0.8423 (346)	13.084 ± 0.088	0.6982 (144)	30.57 ± 0.32	0.5997 (656)	49.17 ± 0.14
			30.36 ± 0.30		
0.8984 (369)	12.896 ± 0.057	0.7910 (164)	29.50 ± 0.45	0.6995 (765)	47.76 ± 0.26
			29.13 ± 0.20		
0.9497 (390)	12.924 ± 0.088	0.8496 (175)	28.17 ± 0.29		
			30.79 ± 0.27		
		0.8984 (185)	29.07 ± 0.37		

[a] In each case the number N of n-mers present in the system is quoted in parentheses. [b] Exact value. [c] This value, obtained by sampling 1.3×10^6 configurations of a simple chain, is an improvement of our preceding estimate: 60.30 ± 0.10.[8]

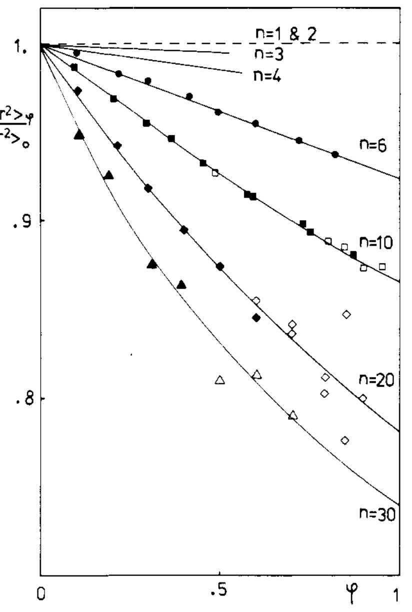

Figure 2. Plot of $\langle r_n^2\rangle_\varphi/\langle r_n^2\rangle_0$ vs. φ for n = 6, 10, 20, and 30. Open dots and full dots respectively correspond to new and old[8] data. The curves represent the least-squares fits obtained with (4). (Initial slopes for n = 3 and 4 are taken from ref 8.)

In the intermediate density region we verified that $\langle r_n^2\rangle$ values obtained from this new generating technique and from the one used previously[8] agree very well for n = 10 and 20. This appears to us as a rather strong test of the validity of the Monte Carlo methods.

Analysis of the Results

The resulting estimates of $\langle r_n^2\rangle$ for n = 10, 20, and 30 are listed in Table I, as a function of the fraction φ of sites occupied by other n-mer chains; i.e., $\varphi = n(N - 1)/V$, where V is the volume of the system (total number of sites). The quoted uncertainties represent the mean-square deviation of the $\langle r_n^2\rangle$ values obtained from different runs (six runs at least of 500 configurations each for n = 10 and 20; ten runs at least of 100 configurations each for n = 30). Figure 2 shows the ratio $\langle r_n^2\rangle_\varphi/\langle r_n^2\rangle_0$ vs. φ; in addition to the new data of Table I, it also includes previous results for n = 6, 10, 20, and 30.[8]

In spite of the long sequences of configurations sampled, one cannot rule out the possibility that at sufficiently high concentration the system gets stuck in a metastable state. As a check two independent series of runs were made in the case n = 20 at three φ values close to 0.7, 0.8, and 0.85, by starting from different initial conditions. The results match each other in the two first instances, but strongly disagree at the highest concentration, showing that the uncertainties quoted in Table I may be unduly optimistic for long chains as φ gets close to one.

At any rate a reasonable conclusion is that the chain contraction, observed for low or intermediate φ values, persists at high concentrations though it appears to slow down. Various least-square fits of the data shown on Figure 2 were attempted. The most satisfactory one corresponded to the purely empirical formula

$$\langle r^2\rangle_\varphi/\langle r^2\rangle_0 = (1 + A\varphi)/(1 + B\varphi) \tag{3}$$

where A and B are adjustable parameters. At low concentrations it reduces to

$$\langle r^2\rangle_\varphi/\langle r^2\rangle_0 \simeq 1 + (A - B)\varphi \tag{4}$$

while for the bulk polymer (φ = 1) one has

$$\langle r^2\rangle_1/\langle r^2\rangle_0 = (1 + A)/(1 + B) \tag{5}$$

The values of A and B, together with their combinations involved in (4) and (5), are listed in Table II for n = 6, 10, 20, and 30, with the corresponding uncertainties. The initial slope ($A - B$) characterizing the decrease of $\langle r^2\rangle$ with φ agrees fairly well with our preceding estimates[8] (also quoted in Table II) so that there is no need to revise expression 2.

Our essential objective will now be to establish as far as possible the behavior of $\langle r_n^2\rangle_1$ for large n. A seemingly reasonable assumption, generalizing (1) is

$$\langle r_n^2\rangle_\varphi \sim (n - 1)^{\gamma(\varphi)} \tag{6}$$

in the asymptotic limit, with $\gamma_{(0)}$ = 1.20. For any given φ, the validity of this expression can be checked by a log–log plot and $\gamma_{(\varphi)}$ can be subsequently obtained from its slope. Note that in (6) we actually use $n - 1$, and not n itself; although in the asymptotic limit this does not make any difference, expression (6) seems more adequate for representing our data as obviously $\langle r_1^2\rangle = 0$ and $\langle r_2^2\rangle = 1$ for all φ.

Log–log plots of $\langle r_n^2\rangle_1/\langle r_n^2\rangle_0$ and $\langle r_n^2\rangle_1$ vs. $(n - 1)$ are shown on Figures 3 and 4. They are reasonably straight and their least-squares analysis leads respectively to

$$\langle r_n^2\rangle_1/\langle r_n^2\rangle_0 \sim (1.135 \pm 0.014)n^{-0.127\pm0.005} \tag{7}$$

$$\langle r_n^2\rangle_1 \sim (1.179 \pm 0.020)n^{1.080\pm0.007} \tag{8}$$

For isolated chains one has[9]

$$\langle r_n^2\rangle_0 \sim (1.068 \pm 0.001)n^{1.20}$$

One gets upon combination with (7)

$$\langle r_n^2\rangle_1 \sim (1.212 \pm 0.016)n^{1.073\pm0.005} \tag{9}$$

in excellent agreement with (8).

Similar plots of $\langle r_n^2\rangle_\varphi/\langle r_n^2\rangle_0$ for the intermediate φ

Table II
Values of the Parameters A and B, as Well as Related Quantities, Determined by Least Squares[a]

n	A	B	σ_A	σ_B	S_{AB}	$A - B$[b]	$(1 + A)/(1 + B)$	$\langle r_n^2\rangle_1$
6	−0.1586	−0.0868	0.0706	0.0743	0.0052	−0.0718 ± 0.0039 (−0.071 ± 0.004)	0.9214 ± 0.0026	6.66 ± 0.02
10	0.0628	0.2280	0.0369	0.0413	0.0015	−0.1652 ± 0.0046 (−0.163 ± 0.003)	0.8655 ± 0.0012	12.79 ± 0.02
20	0.0762	0.3788	0.0858	0.103	0.0088	−0.303 ± 0.018 (−0.28 ± 0.01)	0.7804 ± 0.0045	28.34 ± 0.19
30	0.459	0.971	0.275	0.333	0.0915	−0.512 ± 0.060 (−0.46 ± 0.006)	0.740 ± 0.016	44.70 ± 0.97

[a] σ_A and σ_B are standard deviations; $S_{AB} = \langle(A - \langle A\rangle)(B - \langle B\rangle)\rangle$. [b] Values between parentheses are preceding estimates obtained by curve fitting at low φ.[8]

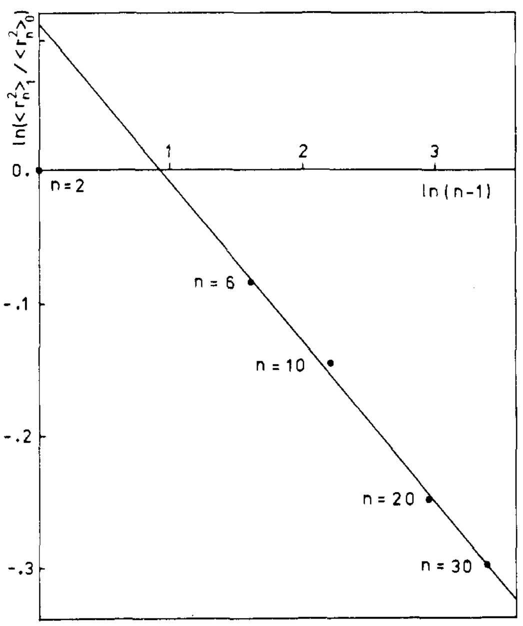

Figure 3. Log-log plot of $\langle r_n^2\rangle_1/\langle r_n^2\rangle_0$ vs. $(n-1)$.

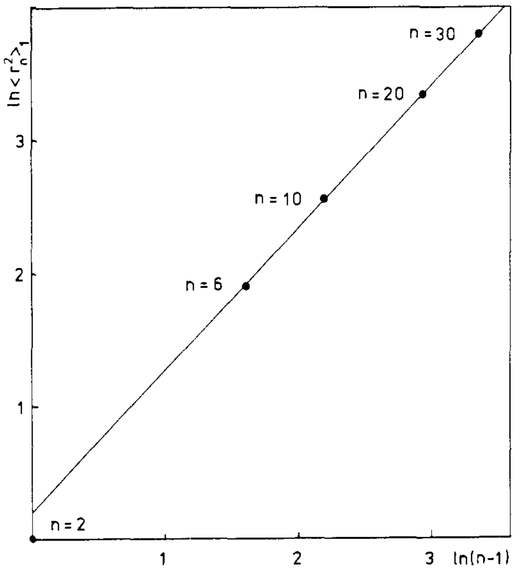

Figure 4. Log-log plot of $\langle r_n^2\rangle_1$ vs. $(n-1)$.

values 0.2, 0.4, 0.6, and 0.8 are almost as straight as those for $\varphi = 1$ and lead to the following estimates of $\gamma(\varphi)$: 1.159, 1.138, 1.105, and 1.087.

Discussion

A tentative conclusion drawn from the data analysis of the preceding section is as follows. For athermal polymer solutions, $\langle r_n^2\rangle_\varphi$ is proportional to $n^{\gamma(\varphi)}$ in the asymptotic limit, with $\gamma_{(\varphi)}$ decreasing monotonously from 1.2 at $\varphi = 0$ to 1.07–1.08 at $\varphi = 1$; according to (8) and (9), our best estimate for the polymer in bulk is

$$\langle r_n^2\rangle_1 \sim (1.20 \pm 0.03)n^{1.075\pm0.010} \qquad (10)$$

We shall now compare these results with theoretical predictions and experimental data.

Mean field theories predict indeed a decrease of $\langle r^2\rangle$ as the polymer concentration increases.[10,11] From the statistical formulation of the expanding factor α of a real chain relative to a gaussian chain, Flory argued that within the bulk phase, a polymer molecule should approach the gaussian behavior, i.e., $\alpha = 1$ and $\langle r^2\rangle \sim n$. His reasoning is rather qualitative; e.g., he states that although a molecule in the bulk state interferes with itself, it has *nothing* to gain by expanding, for the decrease in interaction with itself is compensated by increased interference with its neighbors.[10] Why the compensation ought to be so exact is not clear to us. Nevertheless Fixman[11] largely confirmed Flory's view by developing an approximate theory of the expansion factor α based on the Born-Green-Yvon formulation of the radial distribution function of the polymer segments; he observed indeed that α goes to unity as φ approaches 1.

Experimental data obtained by neutron diffraction of deuterated polystyrene (PSD) dispersed in an undeuterated polystyrene matrix (PSH) have been recently made available by Cotton et al.[12-14] The momentum transfer dependence of the scattering intensity indicates that for the bulk phase[13]

$$\gamma = 1.00 \pm 0.04 \qquad (11)$$

Also, the Zimm-curve analysis leads to the following observations:[12,14] (i) the second virial coefficient A_2 of PSD *within the PSH matrix* is zero; (ii) the mean dimensions of PSD chains are the same as in a Θ solvent. The ensuing conclusion of the authors is that a chain in the bulk phase has recovered its gaussian distribution, i.e.,

$$\gamma = 1 \qquad (12)$$

Let us first point out that the fact that A_2 is zero strictly provides no information about the conformation of the chains in the bulk phase, it just expresses the obvious fact that a deuterated chain is impeded by another deuterated chain exactly in the same way as it is impeded by an undeuterated chain. Hence the essential information obtained from these experiments is (11) and (12), which seemingly agree with approximate theories. In order to allow a better comparison with our own estimate of (10), i.e., $\gamma = 1.075 \pm 0.010$, we submitted the data displayed in Table VI of ref 14 to least-squares analysis. This table gives the mean radius of gyration $\langle S^2\rangle^{1/2}$ of a PSD chain as a function of its molecular weight M in the bulk phase and in cyclohexane at 36° (Θ solvent). Two least-squares fits of these data were carried out, the first one based on

$$\ln \langle S^2\rangle = A + \gamma \ln M \qquad (13a)$$

and the second one based on

$$\langle S^2\rangle^{1/2} = KM^{\gamma/2} \qquad (13b)$$

(These two fits weight the data somewhat differently.) The estimated values of γ are listed in Table III. Independently from the fact that cyclohexane at 36° may or not behave exactly as a Θ solvent, which seems somewhat debatable,[14] the values obtained for γ appear significantly higher than 1 for the bulk phase, i.e.,

$$\gamma \simeq 1.07 \pm 0.03 \qquad (14)$$

in fair agreement with (10) and in slight contradiction with the value in (11) reported by the same authors in another publication.[13]

We are ready to accept that our own estimate of γ for the bulk phase is not necessarily as accurate as it might appear

Table III
Values of γ Obtained from the Data of Table VI of Reference 14 by Least-Squares Fitting

	Cyclohexane (Θ solvent)	Bulk phase
Eq 13a	0.96 ± 0.02	1.06 ± 0.03
Eq 13b	0.98 ± 0.03	1.08 ± 0.04

from (10) as we cannot completely exclude the possibility that the chains considered in our calculations were too short for determining the right asymptotic behavior or even that the data themselves were not as reliable as expected at high concentrations. We nevertheless consider that the value reported here for γ does not really conflict with the neutron diffraction data and that the claim, found in the literature, that intra- and intermolecular interaction *exactly* balance each other for the bulk polymer cannot be regarded as well established at the present time.

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Theoretical Determination of Helix–Coil Parameter σ from a Model of Partly Helical Polypeptide Chain

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ABSTRACT: The Zimm and Bragg parameter σ is calculated numerically for poly(L-alanine), polyglycine, and the copolymers of L-alanine and glycine using the molecular theory of s and σ as developed by Go, Go, and Scheraga in a modified formulation. In this formulation, σ is obtained from the partition function of the whole chain in the helix–coil transition region and represents therefore the contributions from the ends of helical and coil sequences and from the interactions between atoms in a coil sequence with those in the neighboring helical sequence. When the parameter σ is calculated numerically from a hard-sphere potential, it appears that steric interactions between atoms in the coil sequence with atoms in the neighboring helical sequence, which have been neglected in previous calculations, contribute significantly to the value of σ. Owing to these interactions the entropy of the coil sequence as well as σ decrease, but the decrease of σ is larger in poly(L-alanine) than in polyglycine, because of the higher flexibility of the monomer in polyglycine. The numerical value of σ for polyglycine compared with that of poly(L-alanine) might be overestimated however by the model presented here due to approximations inherent in the hard-sphere treatment and because only regular helical sequences are considered.

One of the most promising ways of predicting the secondary structure of proteins is the calculation of helical profiles from the partition function of the chain using Zimm and Bragg parameters s and σ for various residues of amino acids.[2] It is therefore of interest to refine the methods of calculation of σ and s.

These parameters can be obtained from the free energies computed with the help of semiempirical potential functions. The enthalpic contribution to σ from helical sequences has been calculated by Brant[3] for poly(L-alanine). A complete molecular theory of s and σ has been developed by Go, Go, and Scheraga.[4] Subsequently, the parameters s and σ for poly(L-alanine) and polyglycine have been computed numerically from this theory.[5,6]

Here we compute σ using this molecular theory in a modified formulation, by deducing σ from a numerically determined partition function for a chain composed of helical as well as coil sequences. Therefore the ends of both the helical and the coil sequences and the interactions between them contribute to σ. In the theory of Go, Go and Scheraga,[5] atoms in the helical sequence are treated to interact at the junction with such atoms in the neighboring coil sequence, whose positions are determined only by the first rotatable dihedral angle in the coil sequence. Interactions are neglected with atoms in the coil sequence separated further from the junctions.

The modified method for the calculation of σ will be presented in section I and will in section III be applied to poly(L-alanine) and to polyglycine and to copolymers of glycine and L-alanine, using a hard-sphere potential.

With this potential it is easy to locate all atoms involved in steric repulsions. Moreover the values of σ computed from a hard-sphere potential are representative of interactions neglected in previous calculations. In particular, the influence of flexibility of glycyl residue on σ will be investigated, by comparing σ for poly(L-alanine) and for polyglycine as well as for sequential copolymers of glycine and L-alanine.

The description of the model representing the partly helical chain is given in section II and the numerical results in section IV. In section V the method of calculation of σ as well as the numerical results are discussed.

I. Method of Calculation of s and σ

Let us consider a partly helical polypeptide chain with a given distribution γ of helical and coil sequences. This distribution contributes to the partition function by a term Z_γ which may be represented formally by the following expression

$$Z_\gamma = u_{i_1} v_{j_1} u_{i_2} v_{j_2} \cdots v_{j_\nu} u_{i_{\nu+1}} = \pi_{(\nu)}[u_{i_k} v_{j_k}] u_{i_{\nu+1}} \tag{1}$$

where u_{i_k} and ν_{j_k} arise from coil and helical sequences containing i_k and j_k residues, respectively; k is the number of