neglect the overlap integrals such as the INDO or MINDO/2 calculation.[4-5] The energy gap between the highest filled and lowest unfilled bands is equal to $\Delta = 5.16$ eV. This value is not unreasonable and is considerably less than the gap calculated with more sophisticated approximations.[3-5] The charge distribution is given in Figure 1. The carbon atom has a negative charge $\delta-$, while the INDO and MINDO/2 calculations yield a slightly positive charge on carbon.[5]

The band structure obtained without neglecting overlap is also shown in Figure 2. Here, the unoccupied bands are larger than the occupied ones. A similar result was obtained by Imamura with a different set of parameters.[3] Therefore, the widening of the upper bands must be due entirely to the inclusion of overlap integrals. The energy gap Δ in this case is equal to 3.67 eV. This value would put polyethylene on the line between semiconductors and insulators. Experimental measurements of conductivity show that polyethylene is an insulator; therefore, the above-mentioned value of Δ seems rather unlikely. The charge distribution is also overestimated (Figure 1). The inclusion of more neighbors in calculating the elements in eq 3 and 4 does not seem to improve the results significantly, as is apparent from Imamura's work. It might be concluded that the results obtained neglecting overlap are more reasonable than the results of the other method.

(ii) Polyglycine. The qualitatively satisfactory results obtained in the case of polyethylene with the first method (overlap neglected) has encouraged us to further test the method on α-helical polyglycine, Figure 3. The energy band structure obtained is shown in Figure 4. This structure is similar to what is obtained from more sophisticated methods of calculation.[5] The energy gap width Δ is equal to 1.4 eV. According to this value polyglycine would be a semiconductor. Qualitatively speaking, this result should not be surprising, since DNA and proteins are known to be semiconductors. The experimental values reported for DNA vary from 1.8 to 5 eV.[7,8] Figure 3 shows the charge distribution. The signs of the charges agree with those obtained from INDO and MINDO/2 calculations.[5] The charges on the C–O bond seem, however, slightly overestimated.

Conclusion

The width of the energy gap between the higher occupied band and the lower unoccupied (conduction) band, Δ, is very sensitive to the parametrization procedures. The first method proposed in this work seems to give reasonable qualitative results. The quality of the calculated band structure might be further improved by properly rescaling the parameters in eq 6 and 7. Although we do not expect this method to give precise energy bands, in general, we do think that it would give a reasonable qualitative description of the electronic structure of the periodic and semiperiodic polymers which may be helpful in interpreting their chemical and physical properties.

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Statistical Mechanics of Random-Flight Chains. III. Exact Square Radii Distributions for Rings

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ABSTRACT: Analytical relations in the form of series containing $(N-1)/2$ terms have been derived for distribution functions of the square radius of gyration S^2 and of its random orthogonal components S_k^2 for random-flight ring chains with an odd number of bonds N. In the limit for $N \to \infty$, the convergence of the infinite series becomes slower as the argument S_k^2 approaches zero; therefore, for the region of very small S_k^2 a different asymptotic formula is recommended. As has been observed for linear chains, the convergence of the distribution functions with growing N to their limiting forms for $N \to \infty$ is fast; however, the distributions for rings are considerably sharper, with their maxima closer to the average values of the arguments, than is the case for linear chains.

The distribution of the square radius of gyration S^2 for random-flight chains is a function of primary importance for any size-dependent property of flexible macromolecules. Whereas many papers[1-11] have been published on analytical properties and numerical solutions of square radius distributions for linear chains, there seem to be no such data on molecules with other structures. During a recent study[12] of the shape characteristics of random-flight chains with various structures it occurred to us that the square radius distribution for ring macromolecules is especially easy to obtain in a simple form; rings with an odd number of bonds were the only structure with the characteristic function lacking branch points in the complex plane. In view of this unique property

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of ring molecules, it seemed worthwhile to investigate their distributions, although the practical usefulness of the results may be limited by lack of experimental data. Also, the trend shown by ring molecules, as compared to linear ones, should be similar to that of branched molecules, which are more difficult to analyze.

For our calculation, we adopt the widely used random-flight model in which the ring macromolecule is approximated by N equivalent points of unit mass connected by N spring-like bonds. The probability distribution of a bond vector r is assumed to be

$$p(\mathbf{r}) = (2\pi\sigma^2/3)^{-3/2} \exp[-(3/2\sigma^2)\mathbf{r}\cdot\mathbf{r}] \quad (1)$$

where σ^2 is the mean-square bond length; *i.e.*, both short- and long-range interactions are neglected. We are interested in the distributions of the square radius $S^2 \equiv S_3^2$ and of its random orthogonal component, S_1^2, as well as of the sum of two random orthogonal components, S_2^2. It has been shown elsewhere[12] that these distributions for ring macromolecules can be written as the integral

$$P(S_k^2) = (2\pi)^{-1}N^k \int_{-\infty}^{\infty} \frac{\sin^k(\theta/2)}{\sin^k(N\theta/2)} e^{i\lambda S_k^2} d\lambda, \quad k = 1, 2, 3 \quad (2)$$

where $\theta = \arccos(1 + i\lambda')$ and $\lambda' = \lambda\sigma^2/3N$. From eq 2 it is apparent that in the interval $0 < \theta < 2\pi$ the denominator of the integrand has $N - 1$ roots of multiplicity k

$$\lambda_m' = 2i \sin^2(m\pi/N), \quad m = 1, 2, \ldots, N-1 \quad (3)$$

Not all the roots are, however, different; for N odd there are only $(N - 1)/2$ different roots of multiplicity $2k$, whereas for N even there are $(N/2) - 1$ roots of multiplicity $2k$ and one root, $\lambda_{N/2}' = 2i$, of multiplicity k. For the sake of brevity, we denote $(N - 1)/2 \equiv N_1$ and $(N/2) - 1 \equiv N_2$.

The nature of these singular points can be better investigated by using another form of eq 2 obtained by substituting Chebyshev polynomials

$$U_n(1 + i\lambda') = \sin[(n + 1)\theta]/\sin\theta \quad (4)$$

Since Chebyshev polynomials are defined only for integer n, eq 2 then yields two different forms depending upon whether N is even or odd

$$P(S_k^2) = (2\pi)^{-1}(N/2)^k \int_{-\infty}^{\infty} e^{i\lambda S_k^2} \times (1 + \tfrac{1}{2}i\lambda')^{-k/2} U_{N_2}^{-k}(1 + i\lambda')\, d\lambda, \quad N \text{ even} \quad (5a)$$

$$P(S_k^2) = (2\pi)^{-1}N^k \int_{-\infty}^{\infty} e^{i\lambda S_k^2}[U_{N_1}(1 + i\lambda') + U_{N_1-1}(1 + i\lambda')]^{-k} d\lambda, \quad N \text{ odd} \quad (5b)$$

Considering now the fact that the Chebyshev polynomials can be decomposed into products

$$U_n(1 + i\lambda') = 2^n \prod_{m=1}^{n} [i(\lambda' - \lambda_m')] \quad (6)$$

where λ_m' is a zero of the polynomial $U_n(1 + i\lambda')$, we note immediately from eq 5 the difference in type of singularities. For N odd, the denominator of the integrand in eq 5b can be written as the kth power of a polynomial of the N_1th order with N_1 different roots given by eq 3. Therefore, the integrand of eq 5b has N_1 poles of order k, and can be easily evaluated by using the residue theorem. On the other hand, for N even, the integrand of eq 5a for $k = 1, 3$ has a branch point, $\lambda_b' = 2i$, in addition to N_2 poles of order k, and the solution of the integral would have to include also the numerical integration along the branch cut. Only for $k = 2$, *i.e.*, in the case of the distribution $P(S_2^2)$, is this branch point replaced by a simple pole so that the residue theorem can be applied again. This convenient behavior of the characteristic function for $P(S_2^2)$ occurs quite generally, and $P(S_2^2)$ can be calculated analytically for linear, starlike, and comblike macromolecules.[12]

Rings with Odd Number of Bonds

From the preceding discussion it follows that for N odd the distribution function $P(S_k^2)$ can be also written as

$$P(S_k^2) = (2\pi)^{-1}N^k 2^{-kN_1} \int_{-\infty}^{\infty} e^{i\lambda S_k^2} \prod_{m=1}^{N_1} [i(\lambda' - \lambda_m')]^{-k} d\lambda \quad (7)$$

with λ_m' given by eq 3. Now we can proceed to evaluate the integral. The integration path can be closed by an infinite counterclockwise semicircle in the upper half of the complex plane, and the integral in eq 7 expressed as the sum of residues[13]

$$P(S_k^2) = \frac{(-i)^{k-1}N^k}{2^{kN_1}(k-1)!} \times \sum_{l=1}^{N_1} \frac{d^{k-1}}{d\lambda^{k-1}} \left\{ e^{i\lambda S_k^2} \prod_{\substack{m=1 \\ m\neq l}}^{N_1} [i(\lambda' - \lambda_m')]^{-1} \right\}\Big|_{\lambda' = \lambda_l'} \quad (8)$$

The incomplete product needed in eq 8 is obtained from eq 2 and 7

$$\prod_{\substack{m=1 \\ m\neq l}}^{N_1} [i(\lambda' - \lambda_m')] = \left(2^{N_1} i \sin\frac{\theta}{2}\right)^{-1} \frac{\sin(N\theta/2)}{\lambda' - \lambda_l'} \quad (9)$$

and its limit (as well as the limits of its derivatives) for $\lambda' \to \lambda_l'$ are then calculated by applying L'Hospital's rule. This procedure yields the following results for the normalized distributions of reduced square radii, $S_{k,r}^2 \equiv S_k^2/(N\sigma)^2$

$$P(S_{1,r}^2) = 12\sum_l (-1)^{l+1} N^2 \sin^2\gamma_l \cos\gamma_l \times \exp(-6N^2 S_{1,r}^2 \sin^2\gamma_l) \quad (10a)$$

$$P(S_{2,r}^2) = 12\sum_l \exp(-6N^2 S_{2,r}^2 \sin^2\gamma_l) \times [12N^4 S_{2,r}^2 \sin^4\gamma_l \cos^2\gamma_l + N^2 \sin^2\gamma_l (4\sin^2\gamma_l - 3)] \quad (10b)$$

$$P(S_{3,r}^2) = 12\sum_l (-1)^{l+1} \cos\gamma_l \times \exp(-6N^2 S_{3,r}^2 \sin^2\gamma_l)\{72N^6 S_{3,r}^4 \sin^6\gamma_l \times \cos^2\gamma_l + 18N^4 S_{3,r}^2 \sin^4\gamma_l (4\sin^2\gamma_l - 3) + N^2 \sin^2\gamma_l [6 + \tfrac{1}{2}N^2 \sin^2\gamma_l (1 - 25N^{-2})]\} \quad (10c)$$

where the summation over l extends from 1 to N_1 and $\gamma_l \equiv l\pi/N$.

In the limit for $N \to \infty$ and $S_{k,r}^2 > 0$, only the terms with finite l are important, and thus the approximations $N \sin\gamma_l \simeq l\pi$ and $\cos\gamma_l \simeq 1$ may be used. The relations for the dis-

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TABLE I
SOME FINITE TRIGONOMETRIC SERIES USEFUL FOR INTEGRATION OF DISTRIBUTION FUNCTIONS GIVEN BY EQ 10[a]

k	$\Sigma(-1)^{m+1}\cos(m\pi/N)$ $\sin^{-2k}(m\pi/N)$	$\Sigma \sin^{-2k}(m\pi/N)$
1	$(1/12)(N^2-1)$	$(1/6)(N^2-1)$
2	$(1/720)(N^2-1)(7N^2+17)$	$(1/90)(N^2-1)(N^2+11)$
3	$(1/30{,}240)(N^2-1)(31N^4+178N^2+367)$	$(1/9450)(N^2-1)(10N^4+103N^2+103)$

[a] The results hold for N odd; the summation over m goes from 1 to $(N-1)/2$.

tribution functions are then simplified to infinite series

$$\lim_{N\to\infty} P(S_{1,r}^2) = 12\sum_l (-1)^{l+1} l^2\pi^2 \exp(-6S_{1,r}^2 l^2\pi^2) \quad (11a)$$

$$\lim_{N\to\infty} P(S_{2,r}^2) = 36\sum_l l^2\pi^2 \times \exp(-6S_{2,r}^2 l^2\pi^2)(4S_{2,r}^2 l^2\pi^2 - 1) \quad (11b)$$

$$\lim_{N\to\infty} P(S_{3,r}^2) = 12\sum_l (-1)^{l+1} l^2\pi^2 \times \exp(-6S_{3,r}^2 l^2\pi^2)(72S_{3,r}^4 l^4\pi^4 - 54S_{3,r}^2 l^2\pi^2 + {}^1/_2 l^2\pi^2 + 6) \quad (11c)$$

Although these series are bound to diverge for $S_k^2 = 0$, their convergence in the region of practical interest is very fast. For instance, in order to guarantee relative accuracy for $P(S_{3,r}^2)$ better than 10^{-6}, one need use only the first term if $S_{3,r}^2 > 0.1$, two terms if $S_{3,r}^2 = 0.05$, and seven terms if $S_{3,r}^2 = 0.015$. However, the numerical calculation in the range of very small $S_{k,r}^2$ becomes difficult because of large round-off errors. In this region it is preferable to use the asymptotic relation derived by the saddle-point method, as has been done for linear chains by Fixman[1] and Coriell and Jackson[5]

$$P(S_{k,r}^2) = \frac{1}{2}(6\pi)^{-1/2} 6^{-k} k^{k+1} \times (S_{k,r}^2)^{-(2k+3)/2} \exp[-k^2/(24S_{k,r}^2)] \quad (12)$$

Owing to the divergence at $S_k^2 = 0$ of the series in eq 11, these limiting relations must not be used for any operations involving integration over S_k^2; in such cases the formulas in eq 10 for finite N have to be used and the limits for $N \to \infty$ subsequently taken. Some trigonometric identities which might be useful for this purpose are given in Table I. They were obtained by comparing the moments $\langle S_{k,r}^{2u}\rangle$ of the distributions $P(S_{k,r}^2)$, eq 10, with the more generally defined moments $\langle Q^u\rangle$, given by eq 6 of ref 12.

The convergence of the reduced distribution functions for ring molecules with increasing N to their limiting form is quite fast. As shown in Figure 1, the distribution function for $N = 15$ is already close to the limiting dependence. For instance, at $S_{3,r}^2 = 0.07$, the deviations of the distributions for $N = 25$, 49, and 99 from the limiting value for $N \to \infty$ are only -0.96, -0.25 and -0.06%, respectively.

The square radius distributions for linear and ring chains with $N \to \infty$ are compared on Figure 2. The data on linear chains are taken from the paper by Fujita and Norisuye.[8] In both cases the square radius coordinate is divided by its average $\langle S_{3,r}^2\rangle$. Even in this reduced plot, the distribution for rings is clearly narrower, approaching zero faster for large values of the argument, with its maximum closer to the average than is the case for linear chains. All of these features become even more apparent in the nonreduced plot

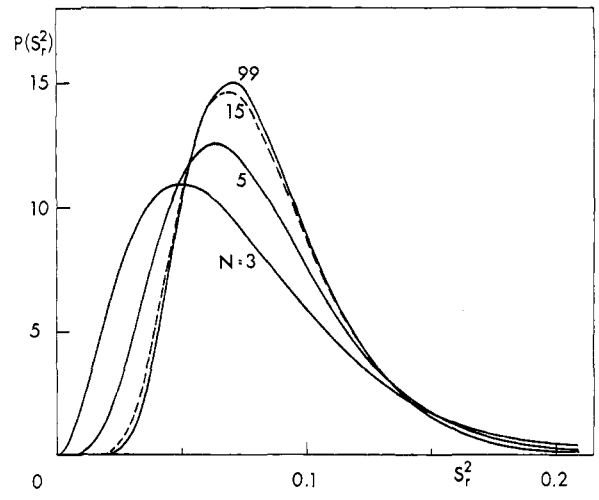

Figure 1. Ring size dependence of the square radius distribution function $P(S^2_{3,r})$. The numbers of bonds are indicated at each curve. On this scale the distributions for $N = 49$ and $N \to \infty$ are indistinguishable from the plotted distribution for $N = 99$.

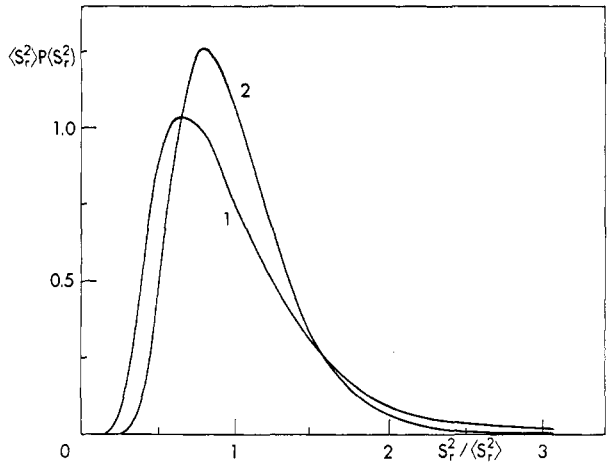

Figure 2. Comparison of the limiting square radius distributions with $N \to \infty$ for linear (1) and ring (2) macromolecules. The dependence for linear chains has been calculated by Fujita and Norisuye.[8]

$P(S_{3,r}^2)$. Obviously, because of the constraint imposed on the ends of a linear molecule by closure to a ring, a ring molecule is much less willing to change its most probable size than a linear one at the same driving force. However, when the chains are being compared in the same medium, the above mentioned effect is overriden by higher segment density in the ring molecule and the ring expands faster than the linear chain, as is indicated by the first-order perturbation theory for both types of chains.[14–16]

Rings with Even Number of Bonds

In this case the simple analytical solution exists only for the two-dimensional distribution function $P(S_2^2)$ given as

$$P(S_2^2) = (2\pi)^{-1} N^2 2^{-N} \int e^{i\lambda S_2^2} \times \left(1 + \frac{1}{2} i\lambda'\right)^{-1} \prod_{m=1}^{N_2} [i(\lambda' - \lambda_m')]^{-2} d\lambda \quad (13)$$

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Using again the residue theorem, we obtain the relation

$$P(S_{2,r}^2) = 12\left\{\frac{1}{2}N^2 \exp(-6N^2S_{2,r}^2) + \sum_l \exp(-6N^2S_{2,r}^2 \sin^2 \gamma_l)[12N^4S_{2,r}^2 \sin^4 \gamma_l \cos^2 \gamma_l + N^2 \sin^2 \gamma_l(4 \sin^2 \gamma_l - 3)]\right\} \quad (14)$$

differing from the corresponding function for N odd, eq 10b, only by the first term and the summation extending from one to N_2. With increasing N the first term diminishes rapidly and goes to zero for $N \to \infty$, as can be expected. Of course both eq 10b and 14 should represent the same family of functions and, accordingly, they can be transcribed in the form which is independent of whether N is even or odd

$$P(S_{2,r}^2) = 6\sum_{l=1}^{N-1} \exp(-6N^2S_{2,r}^2 \sin^2 \gamma_l) \times [12N^4S_{2,r}^2 \sin^4 \gamma_l \cos^2 \gamma_l + N^2 \sin^2 \gamma_l(4 \sin^2 \gamma_l - 3)] \quad (15)$$

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Three-Dimensional Conformations of Polypeptide Chains by Monte Carlo Calculation. I. Model for Random-Coil Conformation

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ABSTRACT: The three-dimensional conformations of polypeptide chains were studied by the Monte Carlo calculation. A simplified model was proposed for the randomly coiled conformation of poly(L-alanine). The conformations generated were classified into "allowed" and "disallowed" conformations, according to the size of the nonbonded interaction energies calculated by use of the Lennard-Jones potential function for pairs of atoms and atomic groups. The chains formed by allowed conformations are equivalent to the "non-self-intersecting chains" usually used. The mean-square end-to-end distance $\langle R^2 \rangle$ and the mean-square radius of gyration $\langle S^2 \rangle$ obtained by taking into account the long-range interaction for randomly coiled chain conformations were essentially consistent with those previously obtained by Monte Carlo calculations based on lattice and nonlattice models. Unperturbed dimensions were also calculated by two different methods. One was a Monte Carlo method in which checking of atomic overlaps was omitted, and the other an exact calculation employing conformational statistics of polymer chains. These unperturbed dimensions were compared with perturbed dimensions obtained by a non-self-intersecting chain model.

Recently statistical-mechanical treatments of polymer chain conformations have been successfully applied to the calculation of unperturbed chain dimension of polypeptides by Flory and his coworkers[1-5] and later by ourselves.[6-8] These theoretical treatments were supported by experimental results.[9-11] Theoretical studies have also been carried out to predict the stability of helical conformations.[12-15] In all the studies mentioned above calculations of conformational energy were performed on the basis of available information on the potential of interaction between nonbonded atoms and atomic groups. The hard-sphere model[16,17] was useful only to classify conformations which are sterically allowed and not allowed. The energy calculation methods using semiempirical potential functions made possible evaluation of the most stable helical structure, and the stability or statistical weight of various conformations in the random-coil state. In the statistical-mechanical treatments of chain conformations and helix–coil transitions, polypeptide chains have been regarded as one-dimensional cooperative systems governed by short-range interactions. Accordingly, the conformational properties obtained there are compared with those observed experimentally in the θ state.

Long-range interactions or excluded volume effects should play an important role in randomly coiled conformations in the nonideal state for biopolymers and their synthetic analogs, by analogy with ordinary polymers. The excluded-volume problems in polymer chains have been studied with the Monte Carlo method by a number of investigators. Wall, *et al.*,[18] have used a method based on the non-self-intersecting random

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