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Statistical Thermodynamics of Nonintersecting Polymer Coils

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ABSTRACT: The methods of statistical thermodynamics were applied to a model of a polymer coil with the following properties. (i) A polymer coil may adopt a finite number of nonintersecting conformations. (ii) Each conformation has a well-defined number of intersegmental contacts. (iii) The contact energy of a coil is proportioanl to the number of contacts. A knowledge of the average number of contacts $\bar{i}(m,x)$ and of the average end-to-end distance $\overline{R^2}(m,x)$ as a function of reduced molecular weight m and of the interaction parameter x is sufficient for calculation of the reduced number of conformations with i contacts and of their average end-to-end distance. Plausible expressions for $\bar{i}(m,x)$ and $\overline{R^2}(m,x)$ were developed.

The size and shape of polymer coils and their dependence on the thermodynamic properties of the solvent have been studied experimentally and theoretically ever since the linear character of polymers was recognized. Nevertheless, the agreement between the theory and the experiment is still not satisfactory. In the present paper we are trying to outline a way to construct a theory, which is sound from the viewpoint of statistical thermodynamics, yet may be adapted to the observed behavior of polymer coils.

Models of Polymer Coils

Most models of polymer coils are based on the recognition of the similarity between the contour of the coil and the trace left by a randomly moving particle. However, there is a basic difference between these two lines: unlike the latter the coil can never intersect itself. Accordingly, we can classify the theories from two viewpoints: (1) how they simulate the random walk problem, and (2) how they handle the problem of self-intersection.

Most theories model the random walk by a succession of steps of fixed length; the angle between two successive steps is often also fixed. Such a model seems inherently satisfactory for description of chemical bonds. However, quite often the steps represent other quantities than chemical bonds. One group of theories places the steps onto a quasicrystalline lattice.[1] The number of possible conformations of the coil on the lattice, while astronomical for long chains, is still limited. For calculations, a specific crystalline lattice must be selected, which is characterized by some coordination number. There is always a problem what part of the computational results should be attributed to the choice of the lattice and/or of coordination number and what part represents the general properties of polymer coils. The lattice points, which are not occupied by separate polymer segments, are filled by solvent molecules.

Another group of theories[2] does not confine the random walk to lattice points and more options are available for each step. In some theories even the length of an individual step is not restricted to a single value: a Gaussian distribution of the step lengths is introduced. This approach seems to avoid some unnecessary restrictions of the lattice model. On the second look, however, this model implies filling of the unoccupied space by continuous solvent: The spatial requirements of the solvent molecules are not considered and the number of possible conformations is grossly exaggerated.

As far as we know, no proper handling of the problem of self-intersection of the coil has been offered.[14] It is obvious that hypothetical conformations of the coil which intersect themselves do not correspond to any physical entity and should be excluded from consideration. Yet their exclusion presents formidable computational problems: The so-called exact enumeration method,[3,4] which excludes them exactly, has been used only for very short chains and its application to long chains is very unlikely. The Monte Carlo techniques

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seem much more promising, but they are also presently limited to medium length chains.[5-7]

All other theories are not addressing the problem directly; they try to compensate for it. The hypothetical self-intersecting conformations are generally tighter than the nonintersecting; their exclusion from statistics yields the average dimensions of coil, which are larger than those obtained when they are retained in the statistics. This apparent deviation from the nonexisting Gaussian coil is compensated by a real effect. The conformations with internal contacts between segments should be weighted in the statistics by a Boltzmann factor reflecting the energy of interaction. The conformations with a larger number of internal contacts are generally tighter than conformations with few or no contacts. When the energy of interaction favors the contacts, the average size of the coil decreases. At some level of the excess energy of contact the two effects are assumed to compensate each other exactly and the system is said to be in a pseudo-ideal theta state. This theta state is considered as a reference state and the individual coils are believed to obey the Gaussian statistics.[2,8] Systems with other values of excess contact energy are evaluated in terms of deviation (expansion) from this reference state. In our opinion, this approach is inherently implausible; too many nonexisting conformations are influencing the statistics.

In the following section we will describe a polymer coil in terms of a distribution function of conformation, which will include only plausible conformations. The analytical form of the distribution function will be left unspecified. It will be shown that some of the interesting features of the distribution function can be deduced from suitable experimental data. In a later section, we will demonstrate the method on an idealized, but experimentally plausible, example.

Statistical Thermodynamics of Nonintersecting Polymer Coils

In the present model we will assume that a polymer coil may adopt a finite number of well-defined nonintersecting conformations. Each conformation will be characterized by a well-defined number of internal contacts i and by its end-to-end distance r. It is convenient to introduce reduced dimensionless variables ρ and m as

$$m \boxminus M/M_0 \tag{1}$$

$$\rho \boxminus r/l \tag{2}$$

where M is the molecular weight of the polymer coil, M_0 is the molecular weight of a characteristic section of the chain, and l is a characteristic length of that section. Let us define $w(m,i,\rho)\,\mathrm{d}\rho$ as a number of conformations of a chain with given values of m and i and with reduced end-to-end distance between ρ and $\rho + \mathrm{d}\rho$. Let us further define $W(m,i)$ as the total number of conformations with given molecular weight and number of contacts and $R^2(m,i)$ as the average reduced end-to-end distance of these conformations; obviously

$$W(m,i) = \int_0^\infty w(m,i,\rho)\,\mathrm{d}\rho \tag{3}$$

$$R^2(m,i)W(m,i) = \int_0^\infty \rho^2 w(m,i,\rho)\,\mathrm{d}\rho \tag{4}$$

For future convenience we will also define the normalized values $W_n(m,i)$ and $R_n^2(m,i)$ as

$$W_n(m,i) \equiv W(m,i)/W(m,0) \tag{5}$$

$$R_n^2(m,i) \equiv R^2(m,i)/R^2(m,0) \tag{6}$$

The energy of a polymer molecule in a conformation with i contacts is in our model defined to be proportional to i. The conformations with no contacts are assigned a reference zero value of energy. The contribution of a single contact to the energy of coil is equal to the negative energy of mixing per contact $(-\Delta\epsilon)$, which is defined in a standard way as

$$\Delta\epsilon \equiv \epsilon_{12} - (\epsilon_{11} + \epsilon_{22})/2 \tag{7}$$

Here ϵ's represent the energy of contact: ϵ_{11} refers to two molecules of the solvent, ϵ_{22} to an intersegmental contact, and ϵ_{12} to a polymer–solvent contact. It is convenient to introduce a new interaction parameter x defined as

$$x \equiv \exp(\Delta\epsilon/kT) \tag{8}$$

where kT has its usual meaning.

Recognizing that the total energy of a coil is equal to $(i\Delta\epsilon)$ we may now write the partition function of conformation $Z(m,x)$ as

$$Z(m,x) = \sum_{i=0}^{\infty} \int_0^\infty w(m,i,\rho) \exp(i\Delta\epsilon/kT)\,\mathrm{d}\rho \tag{9}$$

or using eq 3, 5, and 8 as

$$Z(m,x) = \sum_{i=0}^{\infty} W(m,i)x^i = W(m,0) \sum_{i=0}^{\infty} W_n(m,i)x^i \tag{10}$$

Let us now calculate the average number of internal contacts $\bar{i}(m,x)$.

$$\bar{i}(m,x) = \sum_{i=0}^{\infty} iW(m,i)x^i/Z(m,x) \tag{11}$$

Recognizing that the sum in eq 11 is related to the derivative of the sum in eq 10 we find

$$\bar{i}(m,x) = x(\partial Z/\partial x)_m/Z \tag{12}$$

Integration of eq 12 at constant m from $x = 0$ to x yields

$$Z(m,x) = Z(m,0) \exp\left(\int_0^x \bar{i}(m,x)x^{-1}\,\mathrm{d}x\right) \tag{13}$$

where obviously

$$Z(m,0) = W(m,0) \tag{14}$$

Our goal is to calculate the values $W_n(m,i)$. When the function $\bar{i}(m,x)$ is known from experiment or from some other consideration, the ratio $Z(m,x)/W(m,0)$ may be obtained from eq 13 and 14 and, then, expanded into a McLaurin series in powers of x with coefficients $c(m,i)$ as

$$Z(m,x)/W(m,0) = \sum_{i=0}^{\infty} c(m,i)x^i \tag{15}$$

Comparison of eq 15 with eq 10 yields the wanted values $W_n(m,i)$ as

$$W_n(m,i) = c(m,i) \tag{16}$$

Let us now proceed to the evaluation of the values $R_n^2(m,i)$ and $R^2(m,i)$. The average square end-to-end distance $\overline{R^2}(m,x)$ is given by

$$\overline{R^2}(m,x) = \sum_{i=0}^{\infty} R^2(m,i)W(m,i)x^i/Z(m,x) \tag{17}$$

Obviously

$$\overline{R^2}(m,x = 0) = R^2(m,0) \tag{18}$$

Using eq 5, 6, 14, and 18 we transform eq 17 into

$$D(m,x) \equiv \overline{R^2}(m,x)Z(m,x)/\overline{R^2}(m,x = 0)W(m,0) = \sum_{i=0}^{\infty} R_n^2(m,i)W_n(m,i)x^i \tag{19}$$

When the function $\overline{R^2}(m,x)$ is known from an experiment or from some other consideration and when the ratio $Z(m,x)/W(m,0)$ is known (e.g., from the above analysis of the function $\bar{i}(m,x)$), then the function $D(m,x)$ may be evaluated and expanded into McLaurin series in powers of x with coefficients $d(m,i)$ as

$$D(m,x) = \sum_{i=0}^{\infty} \mathrm{d}(m,i)x^{i} \tag{20}$$

Comparison of eq 19, 20, and 16 yields

$$\mathrm{d}(m,i) = R_{\mathrm{n}}^{2}(m,i)W_{\mathrm{n}}(m,i) \tag{21}$$

$$R_{\mathrm{n}}^{2}(m,i) = \mathrm{d}(m,i)/c(m,i) \tag{22}$$

The un-normalized values $R^2(m,i)$ are easily calculated from eq 6 realizing that knowledge of $\overline{R^2}(m,x)$ implies knowledge of $R^2(m,0)$ by eq 18.

In summary, the knowledge of the functional forms of the average functions $\bar{i}(m,x)$ and $\overline{R^2}(m,x)$ is sufficient for the calculation of all the values of $W_{\mathrm{n}}(m,i)$ and $R^2(m,i)$. However, because the functions $W_{\mathrm{n}}(m,i)$ and $R^2(m,i)$ have a direct physical significance, we must put restrictions on the functions $\bar{i}(m,x)$ and $\overline{R^2}(m,x)$. Namely, only such function $\bar{i}(m,x)$ is acceptable that yields values of $W_{\mathrm{n}}(m,i)$, which are all positive, represent a smooth function of the number of contacts, and vanish at high values of i. The function $\overline{R^2}(m,x)$ should yield values of $R_{\mathrm{n}}^2(m,i)$, which are all positive and represent a smooth, monotonically decreasing function of i. In the following section we will demonstrate the above procedures using functions $\bar{i}(m,x)$ and $\overline{R^2}(m,x)$, which are arbitrarily selected, but which may be quite realistic from the experimental viewpoint.

A Tentative Model of Experimental Behavior. Let us first consider the physical significance of the parameter $\Delta\epsilon$. The standard statistical treatment using the Boltzmann factor, as embodied in our eq 9, 11, and 17, requires $\Delta\epsilon$ to represent energy. In the original Flory–Huggins theory,[8] which considered the combinatorial entropy as the sole part of the entropy of mixing, $\Delta\epsilon$ was related to the parameter χ (experimentally accessible within the frame of Flory–Huggins theory) as

$$\chi = z_0\Delta\epsilon/kT \tag{23}$$

where z_0 is the coordination number of a molecule of the solvent. Later, Flory[8] has argued that there may exist other contributions to the entropy of mixing and that the interaction term $(1/2 - \chi)$ should be replaced by $\psi(1 - \theta/T)$. Consequently, the quantity $\Delta\epsilon$ may itself have the character of free energy. However, in the present context the character of $\Delta\epsilon$ is of no consequence.

It is worthwhile to consider several significant values of $\Delta\epsilon$ and x. (i) In the limiting case of an extremely good solvent, $\Delta\epsilon$ approaches minus infinity, x equals zero, and all polymer molecules adopt conformations without any internal contacts. (ii) For a regular solvent, $\Delta\epsilon$ is equal to zero, x equals one, and all the Boltzmann factors degenerate to unity. (iii) The pseudo-ideal theta conditions correspond to some special values $\Delta\epsilon_\theta$ and x_θ. (iv) In the limiting case of an extremely poor solvent, both $\Delta\epsilon$ and x approach infinity, and all polymer molecules adopt conformations with the maximum possible number of internal contacts $i_{\max}(m)$, i.e., they form compact spheres. (It should be noted that we are considering isolated polymer chains. In solutions with finite concentrations, some finite value of x will cause phase separation before the coils collapse fully.)

Let us now proceed to designing the function $\overline{r^2}(m,x) \equiv l^2\overline{R^2}(m,x)$. We will base our model on intrinsic viscosity $[\eta]$ which is a rather sensitive measure of the molecular dimensions as is apparent from the well-known relation[8]

$$[\eta] = \phi(\overline{r^2})^{3/2}/M \tag{24}$$

The Flory's constant ϕ is only slightly dependent on the polymer–solvent interaction. It has been repeatedly found experimentally that for molecular weights, which are not too low (e.g., they are higher than about 30 000 for typical vinyl polymers), the dependence of $[\eta]$ on molecular weight may be described very accurately by the Mark–Houwink–Sakurada relation[9]

$$[\eta] = K_\eta M^{a_\eta} \tag{25}$$

The parameters K_η and a_η depend on the polymer–solvent interaction.

The combination of eq 24 and 25 as well as numerous experimental light-scattering data[10] suggest that $\overline{r^2}$ is a power function of molecular weight (provided that the molecular weight is high enough). The Monte-Carlo calculations lead to the same conclusion.[7] The bilogarithmic plot of $\overline{r^2}$ vs. M is linear; the lines for the same polymer in two solvents with a different solvent power intersect in the region of low molecular weights (beyond the region of validity of the power function). In our previous paper[9] we have shown that in an analogous plot of $[\eta]$ vs. M for the same polymer in a series of solvents all the intersection points are closely clustered at about M = 5000 (for polystyrene and poly(methyl methacrylate)). To model this behavior, we will assume that all these lines intersect at a single point with coordinates M_0 and l.[2] Further, we will identify these M_0 and l with the characteristic values, which were used in definitions of the dimensionless variables m and ρ, eq 1 and 2. Consequently, we postulate

$$\overline{R^2}(m,x) = m^{a(x)} \tag{26}$$

where the exponent $a(x)$ is a function of the interaction parameter x.

Now, we need to postulate the functional form of $a(x)$. Experimentally, the exponent varies in a remarkably narrow range for a large number of good and intermediate solvents. However, as the solvent power gets poorer, the exponent is decreasing ever steeper and the coil suddenly collapses within a narrow range of values of the interaction coefficient. Such behavior is observed, for example, when the temperature is lowered in a close vicinity of the theta temperature.[11] Similar behavior was observed also in Monte-Carlo calculations.[7] In the region of still higher x, the decrease should slow down and the exponent should eventually reach the value of $2/3$, which is characteristic for compact bodies. However, the latter behavior has not been actually observed; the phase separation in real experiments always precedes the full collapse of the coil. To simplify the mathematical analysis, we will assume that the exponent $2/3$ is reached already at some finite value x_c; the values of $x > x_c$ will be considered as physically meaningless. We will see later that this simplification will lead to some unreasonable values of $W_{\mathrm{n}}(m,i)$ and $R_{\mathrm{n}}^2(m,i)$ for the values of i corresponding to the region of fully collapsed coil. However, they do not influence seriously the bulk of $W_{\mathrm{n}}(m,i)$ and $R_{\mathrm{n}}^2(m,i)$ data.

Using this simplification, we model the experimental behavior by postulating $a(x)$ as a hyperbolic function with parameters a_0, β, γ

$$a(x) = a_0 + \beta - \beta/(1 - \gamma x) \tag{27}$$

The parameter a_0 is actually the exponent $a(0)$ for an infinitely exothermic solvent. The parameters β and γ will be calculated from a_0, from an exponent for a regular solvent $a_{\mathrm{R}} = a(1)$, and from the value of x_θ, for which, by definition, $a(x_\theta) = 1$. We will also calculate x_c for which $a(x_c) = 2/3$. A straightforward calculation yields

$$\beta = (a_0 - a_{\mathrm{R}})(a_0 - 1)(x_\theta - 1)/[(a_0 - 1) - (a_0 - a_{\mathrm{R}})x_\theta] \tag{28}$$

$$\gamma = [1 - (a_0 - a_{\mathrm{R}})(x_\theta - 1)/(a_{\mathrm{R}} - 1)]/x_\theta \tag{29}$$

$$\begin{aligned} x_c &= (3a_0 - 2)/\gamma[3a_0 - 2 + 3\beta] \\ &= (3a_0 - 2)(a_{\mathrm{R}} - 1)/[(a_0 - 1)(3a_{\mathrm{R}} - 2)/x_\theta - (a_0 - a_{\mathrm{R}})] \end{aligned} \tag{30}$$

Table I
Characteristic Parameters of the Model

a_0	1.22	γ	0.912049
a_R	1.20	β	0.001929
		x_G (χ = 0.4)	1.068939
z_0	6	x_θ	1.086904
z_p	4	x_c	1.092624
z_s	1	α	100.0
n	50	α_1	0.32817

It remains to specify x_θ. Recalling that for theta conditions $\chi = 1/2$, we find from eq 8 and 23

$$x_\theta = \exp(1/2z_0) \qquad (31)$$

The above model of the function $\overline{R^2}(m,x)$ followed closely the available experimental data. Unfortunately, we do not know about any experimental data which would yield a direct estimate of the other basic function, $\bar{i}(m,x)$. It is necessary to use a different approach. One possible approach is the so-called "smoothed density" model, which is used by many theories.[8,12] The time average of the concentration (density) of polymer segments in each volume element is considered instead of its actual value. As the molecular weight gets higher, the averaged concentration of segments gets lower. Consequently, the chance that a given segment is in contact with some other segment is decreasing. We do not espouse this concept. In the region of the coil most volume elements are empty. The presence of a segment leads to the presence of other segments; the local concentration is higher than time-averaged concentration in the vicinity of most segments and their chance of being in contact does not decrease with increasing molecular weight.

In the present approach we will introduce the maximum number of contacts which can be formed by a given coil $i_{\max}(m)$. For its calculation we will divide the characteristic section with molecular weight M_0 into n segments, each of them having an effective volume a^3 and z_p contact sites. The maximum number of contacts is realized, when the coil collapses into a sphere; it equals one-half of all contact sites $nmz_p/2$ minus one-half of the contact sites, which are located on the surface of the sphere. Assuming that a surface segment requies an effective surface area a^2 and has z_s "outward" contact sites, we find that the number of the surface contact sites is $z_s(36\pi n^2m^2)^{1/3}$. Finally, we get for $i_{\max}(m)$

$$i_{\max}(m) = \alpha m(1 - \alpha_1 m^{-1/3}) \qquad (32)$$

$$\alpha = nz_p/2 \qquad (33)$$

$$\alpha_1 = (z_s/z_p)(36\pi/n)^{1/3} \qquad (34)$$

Lacking at the present time any experimental information about the function $\bar{i}(m,x)$ we will design it in such a way as to make $\bar{i}(m,0) = 0$ and $\bar{i}(m,x_c) = i_{\max}(m)$. Moreover, we will require that it satisfies all the requirements enumerated at the end of the section Statistical Thermodynamics.

The function $\bar{i}(m,x)$ defined by eq 35 has all the required properties

$$\bar{i}(m,x) = \frac{\gamma x}{1 - \gamma x}\left[\frac{B(m)}{1 - \gamma x} + 1\right] \qquad (35)$$

$$B(m) \equiv \left[\frac{(1 - \gamma x_c)i_{\max}(m)}{\gamma x_c} - 1\right](1 - \gamma x_c) \qquad (36)$$

For simplicity, the parameter γ is identified with the parameter γ defined by eq 29. Substituting eq 35 into eq 13 we obtain for the partition function

$$Z(m,x)/W(m,0) = \exp\left(\frac{B(m)\gamma x}{1 - \gamma x}\right)\Big/(1 - \gamma x) \qquad (37)$$

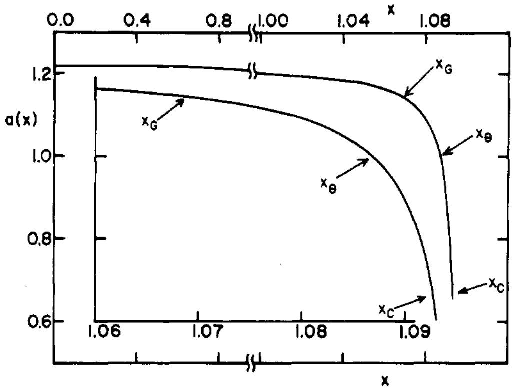

Figure 1. The exponent $a(x)$ as a function of parameter x. In the insert the more relevant section is plotted using an expanded scale. The arrows correspond to good (G), theta (θ), and critical (c) solvent, respectively.

Expanding eq 37 into series and using eq 15 and 16 the following expression for $W_n(m,i)$ is obtained

$$W_n(m,i) = \gamma^i \sum_{j=0}^{i} \frac{[B(m)]^j}{j!}\binom{i}{j} \qquad (38)$$

where a standard notation is used for factorials and binomial coefficients. To obtain the values of $R_n^2(m,i)$, the relations 26, 27, and 37 are substituted into eq 19 yielding

$$D(m,x) = \exp\left[\frac{(B(m) - \beta \ln m)\,\gamma x}{1 - \gamma x}\right]\Big/(1 - \gamma x) \qquad (39)$$

its expansion into series and use of eq 20 and 21 then gives

$$R_n^2(m,i)W_n(m,i) = \gamma^i \sum_{j=0}^{i} \frac{[B(m) - \beta \ln m]^j}{j!}\binom{i}{j} \qquad (40)$$

The values of $R_n^2(m,i)$ are obtained by dividing eq 40 and 38.

Results

The values for numerical calculations were selected as follows: The exponents $a_0 = 1.22$ and $a_R = 1.20$ are based on the Monte Carlo calculations;[7] they are well acceptable from experimental viewpoint. The coordination numbers are those which are applicable to a simple cubic lattice: $z_0 = 6$, $z_p = 4$, $z_s = 1$. For the number of segments per characteristic section we have selected $n = 50$; for vinyl polymers there are typically 5–6 monomer units per statistical segment and about 9 statistical segments per characteristic section.[9] The values of derived quantities are collected in Table I. For illustrative purposes the value x_G for a typical good solvent with $\chi_G = 0.4$ is included; it is defined as

$$x_G \equiv \exp(\chi_G/z_0) \qquad (41)$$

The exponent $a(x)$ calculated from the values in Table I is plotted in Figure 1; in the insert the data relevant for typical good and poor solvents are plotted using an expanded scale. The arrows correspond to good ($\chi_G = 0.4$), theta, and critical solvent, respectively.

Using eq 38 we have calculated the values $W_n)m,i)$ for several values of m. In Figure 2 log $W_n(m,i)$ is plotted as a function of i. For low molecular weights log $W_n(m,i)$ is monotonically decreasing with increasing i; for higher m it exhibits a maximum at a value of i, which is quite close to $\bar{i}(m,x = 1)$ as calculated from eq 35. The normalized number of molecules adopting a conformation with i contacts is proportional to $x^iW_n(m,i)$. This quantity is plotted using a bilogarithmic scale as a function of i in Figure 3 for a polymer chain with $m = 300$ and the values of $x = 1$, $x = x_G$, $x = x_\theta$, and $x = x_c$, respectively. For higher values of x, the dependences

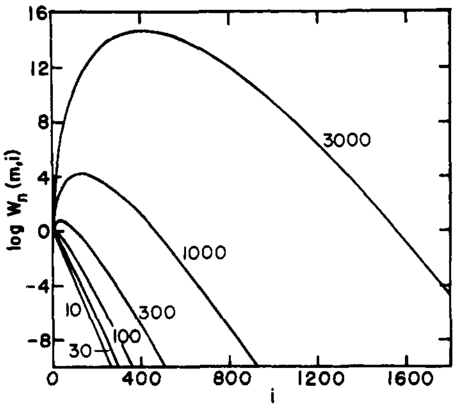

Figure 2. Log $W_n(m,i)$ as a function of number of contacts. The curves are labeled by the value of reduced molecular weight m.

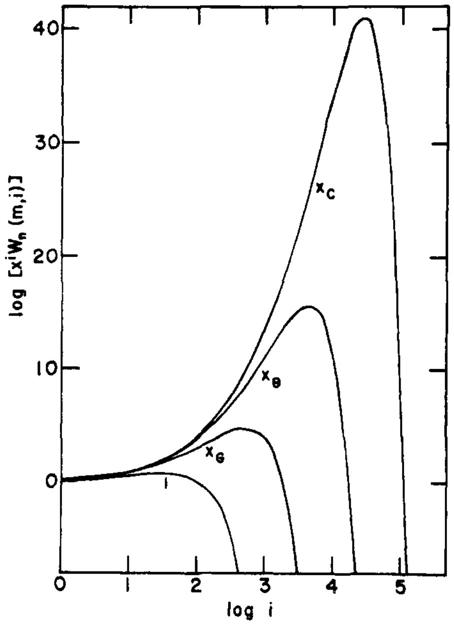

Figure 3. The normalized number of molecules with i contacts $x^iW_n(m,i)$ as a function of the number of contacts in a bilogarithmic scale for m = 300. The curves are labeled by the value of x.

exhibit a sharp peak (note the scale of the ordinate) at values of i, which are again quite close to $\bar{i}(m,x)$.

The values of $R_n^2(m,i)$ were calculated for several values of m using eq 38 and 40. They are plotted as a function of i in Figure 4. The decrease of the size of the coil is sharpest for first contacts and surprisingly it is largest for chains with $m \approx 100$. For larger number of contacts, the decrease of size with the number of contacts is much less pronounced; the relative decrease per contact gets larger as the molecular weight gets lower. In Figure 5 the logarithm of the normalized number of molecules adopting a conformation with i contacts $x^iW_n(m,i)$ is plotted as a function of the reduced end-to-end distance $R_n^2(m,i)$ for m = 300 and for $x = 1$, $x = x_G$, $x = x_\theta$, and $x = x_c$, respectively. The dependences exhibit peaks corresponding to appropriate values of $R^2(m,x)/R^2(m,0)$.

Discussion

The method described above in the section "Statistical Thermodynamics" for obtaining the normalized values $W_n(m,i)$ and $R_n^2(m,i)$ from the experimental functions is based strictly on the accepted rules of statistical thermodynamics and is, therefore, valid within the limits of statistical thermodynamics. The only assumptions made in the treatment were that the number of internal contacts is well defined and that each contact contributes the same increment to the energy of the system without regard to the number of existing contacts. However, it is necessary to discuss two questions related to our tentative model of polymer behavior: (i) How well do our relations represent the behavior of real polymer solutions? (ii) Are the calculated values of $W_n(m,i)$ and $R_n^2(m,i)$ unique for systems obeying (within the experimental error) the prescribed functions $\bar{i}(m,x)$ and $\overline{R^2}(m,x)$? Let us address the second question first.

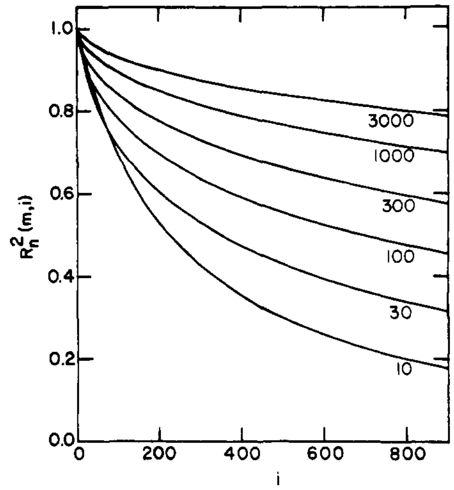

Figure 4. $R_n^2(m,i)$ as a function of number of contacts. The curves are labeled by the value of m.

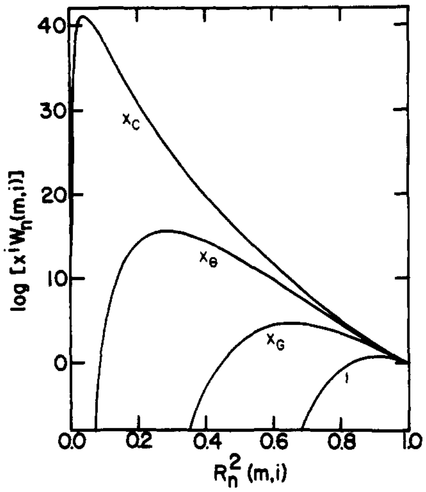

Figure 5. The value of log $[x^iW_n(m,i)]$ as a function of reduced end-to-end distance $R_n^2(m,i)$ for m = 300. The curves are labeled by the value of x.

In our development we have started from the expression for $\bar{i}(m,x)$; the expression for the partition function $Z(m,x)$ was obtained by integration according to eq 13. The operation of integration tends to reduce the differences between functions, which differ very little: if the expression for $\bar{i}(m,x)$ represents the real function well enough, so does the expression for $Z(m,x)$. However, during calculation of $W_n(m,i)$ from $Z(m,x)$ according to eq 15 and 16 multiple differentiation is required, i.e., an operation which vastly amplifies the differences between similar functions.

It is a well-known fact that any function may be approximated within deliberately small deviation by a large number of analytical expressions, which may be quite dissimilar to each other. When developed into McLaurin series these expressions may lead to wildly dissimilar sets of coefficients. To remove the ambiguity we have required that the sets of coefficients $W_n(m,i)$ and $R_n^2(m,i)$ represent a smooth nonnegative function of the number of contacts i. Is this requirement strong enough to assure that the coefficients are accurate within an acceptable (i.e., deliberately small) error? In the Appendix we present an argument, which answers this question in the affirmative.

Let us now return to the question whether the suggested relations are reasonable. The dependence of $W_n(m,i)$ on its arguments is based on rather speculative relations, eq 35 and 36. As is apparent from Figures 2 and 3, these relations imply that the average number of internal contacts is rather high, especially for higher molecular weights and/or poorer solvents. We find such concept quite plausible: after all even the smoothed density model, which underestimates the number of contacts, predicts quite a large number of contacts, and the number of contacts in a real, fully collapsed coil *is* huge. We also consider as gratifying the fact that the partition function is an exponential function of $B(m)$ and, through it, of $i_{\max}(m)$, and of m (eq 37, 36, and 32). This corresponds nicely with the observation of McCrackin, Mazur, and Guttman[7] which was based on Monte-Carlo simulations, namely that the partition function per segment is essentially independent of the number of segments for chains, which are long enough, and for all values of parameter x.

An obvious inadequacy of our function $\bar{i}(m,x)$ is the assumption that at some finite value x_c the average number of contacts is equal to the maximum possible number of contacts. This assumption is related to a corresponding assumption that at $x = x_c$ the average size of the coil is the most compact size. These assumptions lead to assigning a nonzero value of $W_n(m,i)$ to values $i > i_{\max}(m)$ (Figure 3). However, $x^i W_n(m,i > i_{\max}(m))$, the number of molecules adopting these impossible conformations is nonnegligible only if the value of x is quite close to x_c. For solvents which are theta or better, the contribution of such conformations is completely negligible.

Our tentative relations, eq 26 and 27, for $\overline{R^2}(m,x)$ were obtained by considerations, which were based on experimental observations: (i) the Mark–Houwink–Sakurada exponent varies in a narrow interval for large number of good solvents; (ii) the value of this exponent decreases sharply with decreasing temperature in the vicinity of theta temperature; the temperature is related to parameter x by eq 8. Consequently, relations 26 and 27 are probably not grossly incorrect. However, they are certainly not valid for very small values of m (e.g., $m < 6$ or 10) and consequently even our values $R_n^2(m,i)$ are meaningless for such values of m. We suspect that even the crossing of lines in Figure 4 is caused by this inadequacy.

The existence of a large number of contacts for polymers in theta solvents throws a new light on the perturbation theory of a Gaussian coil. It seems that a calculation of the probability that two far-apart segments are in contact must be virtually intractable due to the fact that the segments in-between are necessarily interconnected by numerous loops.

Conclusions

The classical statistical thermodynamics of a nonintersecting polymer coil with internal contacts when applied to our tentative model of experimental behavior produced plausible values for the normalized number of conformations $W_n(m,i)$ and normalized end-to-end distance $R_n^2(m,i)$ for chains with the reduced molecular weight m and number of internal contacts i. From the analysis, several observations came forth, which may not have been fully appreciated previously: (i) The average number of internal contacts within the coil is very high, especially at high molecular weights and/or with poorer solvents. (ii) The normalized number of conformations is a monotonically decreasing function of the number of contacts for small molecular weights but exhibits a maximum for large molecular weights. (iii) The change of the average end-to-end distance, when the number of contacts increases by one, is very small, especially when already many contacts are formed. (iv) The Boltzmann factors involved (eq 9) are huge (a small change in the interaction parameter x leads to a rather spectacular shift in the occupancy numbers for conformations with different numbers of contacts).

In the present treatment, we were able to analyze only (i) the total number of conformations with given molecular weight and number of contacts and (ii) their average end-to-end distance. The more basic function $w(m,i,\rho)$ cannot be obtained from this analysis. The further progress could be achieved in two directions. First, the form of the functions $\overline{R^2}(m,x)$ and $\bar{i}(m,x)$, which were designed rather arbitrarily in this paper, could be improved using appropriate experiments. Second, the standard Monte-Carlo simulation method for nonintersecting chains could be amended in such a way as to follow also the statistics of internal contacts in detail with the aim of obtaining the function $w(m,i,\rho)$.

We would like also to note that the whole analysis would remain formally identical if the symbol r is understood to mean radius of gyration instead of the end-to-end distance.

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Appendix

Let us consider two analytical functions, $F_1(x)$ and $F_2(x)$, which differ only insignificantly within some finite range of x values, $x \in \langle a,b \rangle$. Both these functions may be developed into McLaurin series as

$$F_1(x) \equiv \sum_{i=0}^{\infty} f_1(i) x^i \qquad \text{(A1)}$$

$$F_2(x) \equiv \sum_{i=0}^{\infty} f_2(i) x^i \qquad \text{(A2)}$$

Both sets of coefficients, $f_1(i)$ and $f_2(i)$, are smooth nonnegative functions of i. Is it possible that the two sets of coefficients differ significantly within some range of values of i? (Note that they cannot differ significantly for only a single value of i, or for a number of isolated values of i, because of the requirement that both sets are smooth functions of i.)

First, let us assume that the two sets are identical except for some relatively narrow region of i values between j and $(j + \Delta j)$. Due to the smoothness of the functions $f(i)$ we may replace them approximately within this narrow region by some average value $\bar{f}(j)$. Then the difference $\Delta(x)$ between the functions $F(x)$ may be written as

$$\Delta(x) \equiv F_2(x) - F_1(x) \doteq [\bar{f}_2(j) - \bar{f}_1(j)] \sum_{i=j}^{j+\Delta j} x^i \qquad \text{(A3)}$$

The difference $\Delta(x)$ is very small by definition. It follows that the difference $[\bar{f}_2(j) - \bar{f}_1(j)]$ must be also very small provided that the region around $i = j$ contributes significantly to the value of $F(x)$ for some value of $x \in \langle a,b \rangle$. Thus, $\bar{f}_2(j)$ must be approximately equal to $\bar{f}_1(j)$ for all such values of j. This contradicts our assumption; consequently, the two sets cannot differ significantly in a single region of values of i.

Next, let us assume that the two sets of $f(i)$ differ significantly in two regions: between j and $(j + \Delta j)$, and between k and $(k + \Delta k)$. Introducing again the average values we obtain

$$\Delta(x) \doteq [\bar{f}_2(j) - \bar{f}_1(j)] \sum_{i=j}^{j+\Delta j} x^i + [\bar{f}_2(k) - \bar{f}_1(k)] \sum_{i=k}^{k+\Delta k} x^i \qquad \text{(A4)}$$

The requirement of $\Delta(x)$ being small calls for a compensation of the first term of eq A4 by the second term. Obviously, when the compensation is achieved for one value of x, it is not good enough for a rather different value of x. Consequently, even the present assumption is contradicted.

The extension of the above argument for three and more regions of $f(i)$ values is obvious. We may, therefore, conclude that the requirement that the McLaurin coefficients form a smooth function of i is a very strong one. It implies that all plausible representations of function $F(x)$, which are subject to this requirement, yield sets of McLaurin coefficients which differ only insignificantly among themselves. The only exception are coefficients of those terms, which do not contribute significantly to the value of $F(x)$ at any value of $x \in \langle a,b \rangle$.

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(14) **Note Added in Proof:** After this paper was submitted for publication, Gordon et al.[13] published a paper using a novel approach for handling the intersegmental contacts. Their method is based on the random walk on the lattice with intersections allowed. The intersections are considered to be local violations of the lattice condition; they represent the contacts. The authors have shown that for this model in the limit for long walks the function $W_n(m,i)$ approaches Gaussian form. The position of the maximum is a linear function of the length of the chain m. Such a behavior is in qualitative agreement with the results presented in our paper; this is apparent from our Figure 2. However, the Gaussian function, if plotted in coordinates of Figure 2, would exhibit a parabolic (i.e., symmetrical) form. Our lines exhibit assymetry which, while decreasing with increasing m, is still very pronounced for $m = 3000$. The discrepancy may be caused by our (arbitrary) choice of the function $\bar{\iota}(m,x)$, eq 35 and 36. However, the difference may also indicate that the limit of long walks must be applied with caution; it is possible that it is applicable only far beyond the region of the interest of a polymer chemist. (Gordon et al.[13] discuss the correction for shorter chains as effecting only the width of the Gaussian curve and not its Gaussian character.) Another difference may be related to the previous one: Gordon et al. predict that the change of the interaction parameter and of the coil expansion is accompanied by a relatively small change in the number of contacts. Our model predicts a massive change, cf. Figure 3. We are grateful to Professor Gordon for directing our attention toward his recent work.

Polymerization of Methyl Methacrylate Photoinitiated by 4,4'-Bis(*N*,*N*-diethylamino)benzophenone. 1

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ABSTRACT: Polymerization of methyl methacrylate (MMA) photoinitiated by 4,4'-bis(*N*,*N*-diethylamino)benzophenone (DEABP) was shown to have unusual kinetic behavior attributable to primary radical termination reactions. This deviation from normal kinetic orders in light intensity, photoinitiator, and monomer concentrations qualitatively parallels observed concentration effects on quantum yield for the photochemical disappearance of Michler's ketone in cyclohexane. Increasing the DEABP concentration, beyond certain limits, lowers the rate of photopolymerization for MMA analogous with lowering of the quantum yield for disappearance of Michler's ketone with increasing concentrations of reactant. Molecular weights of the photopolymerized samples are significantly lower than for thermally initiated polymerizations using azodiisobutyronitrile (VAZO-64) as initiator. It is also shown that DEABP (ground state) does not influence the rate of polymerization or the molecular weight distribution of VAZO-64 thermally initiated polymerization of methyl methacrylate. Multiple detector GPC/IR/UV examination of thermally polymerized MMA showed no fragments of DEABP attached to the polymer backbone thus eliminating the possibility of growing polymer radical chain transfer to the ground state photoinitiator. Analysis of the photopolymerized MMA by GPC/IR/UV multiple detection does show photoinitiator or photoproduct fragments attached to the polymer backbone and accounts for the observed lowering of molecular weights (initiation as well as primary radical termination). Broadening of the molecular weight distribution (monomodal to almost bimodal) for the photopolymerized MMA between narrow DEABP concentration ranges indicated a change in photoinitiation mechanism. Drastic solvent effects (nonpolar–polar) were observed for the photoinitiated polymerization of MMA using DEABP initiator. Polymer formation decreased as the polarity and reactivity of the solvent–MMA mixtures were changed from benzene (polymer formed), cyclohexane (little polymer formation), and methanol (no polymer formed). These results are attributable to the decrease in the quantum yield for intersystem crossing efficiency (ϕ_{st}) of aminoaromatic ketones (Michler's ketone) as the polarity and reactivity of the solvent changes. Reaction mechanisms and kinetic schemes, consistent with the experimental observations, are presented and discussed.

In the past 10 years, an intensive industrial effort has been directed toward pollution-free coatings. The area of ultraviolet-initiated polymerization (photoinitiated cure) has grown considerably, especially with the commercialization of ultraviolet curable inks and wood coatings. The rapid increase of patent literature on new photoinitiators and radiation curable coating systems is strong indication that photopolymerization will be a very important pollution-free curing process in the near future.

The use of 4,4'-bis(*N*,*N*-dimethylamino)benzophenone (Michler's ketone) and benzophenone as photoinitiators for the photopolymerization of vinyl unsaturation have been disclosed in the recent patent literature.[1–4] The photophysical processes involved or associated with the photochemistry of

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