$$j_l(\mu \mathbf{R}_{ij}) C_\lambda^l(\hat{\mathbf{R}}_{ij}) = \frac{(-i)^l}{4\pi} \int \mathrm{d}\mathbf{K} e^{i\mathbf{K}\cdot\mathbf{R}_{ij}} C_\lambda^l(\hat{\mathbf{K}}) \frac{\delta(\mu - K)}{\mu K} \tag{C.1}$$

where $\delta(x)$ is the Dirac δ function. But, we have

$$\mathbf{R}_{ij} = \mathbf{R}_{\alpha\beta} + \mathbf{b}_{\alpha i} - \mathbf{b}_{\beta j} \tag{65}$$

Therefore, replacing and making repeated use of Rayleigh's expansion formula (eq 39), we get, after much algebra

$$\begin{aligned} j_l(\mu \mathbf{R}_{ij}) C_\lambda^l(\hat{\mathbf{R}}_{ij}) = {} & (-i)^l \sum_{rst} (i)^{r+s+t} (2r + 1)(2s + 1)(2t + 1) \times \\ & j_r(\mu \mathbf{b}_{\alpha i}) j_s(\mu \mathbf{b}_{\beta j}) j_t(\mu \mathbf{R}_{\alpha\beta}) \sum_{p\sigma\tau} C_p^r(\hat{\mathbf{b}}_{\alpha i}) C_\sigma^s(\hat{\mathbf{b}}_{\beta j}) \times \\ & C_\tau^t(\hat{\mathbf{R}}_{\alpha\beta}) (-)^\tau \sum_{j,\zeta} (2j + 1) \begin{pmatrix} r & s & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} t & l & j \\ 0 & 0 & 0 \end{pmatrix} \times \\ & \begin{pmatrix} r & s & j \\ p & \sigma & -\zeta \end{pmatrix} \begin{pmatrix} t & l & j \\ \tau & \lambda & \zeta \end{pmatrix} \end{aligned} \tag{C.2}$$

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The Determination of Chain Statistical Parameters by Light Scattering Measurements

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ABSTRACT: The effects of volume exclusion on polymer chain conformations can be determined from the study of the angular dependence of radiation scattered by chain molecules. It is found that useful information can be obtained only when the variable x is large, where x is the product of the square of the magnitude of the scattering vector and of the mean square radius of gyration. Hence, solutions of macromolecules of very high molecular weight are needed for these investigations. The theoretical treatment of the scattering function is based on several assumptions. The validity of these assumptions is examined by computing, using a Monte-Carlo technique, various moments of intramolecular separations and comparing the results so obtained, in the limit of a chain of infinite length, with the analytical results. The computations seem to verify the validity of the theoretical model. The scattering behavior of solutions of recently synthesized polystyrene of $M_w = 4.4 \times 10^7$ in cyclohexane at various temperatures and in benzene at 40° was investigated. From the log–log plots of the scattering function vs. x, a statistical parameter was calculated, whose value depends on the magnitude of long-range correlations between any pair of chain elements. It is found that above the Θ temperature this parameter is practically independent of temperature and that its numerical value was found to agree well with the value obtained from Monte-Carlo calculations. In the neighborhood of the Θ temperature, this parameter decreases rapidly with decreasing temperature, indicating a first-order transition in chain conformation.

I. Introduction

A. Experimental Background. Since the introduction of Debye's analysis[2] of molecular light scattering measurements, it has been the mainstay of exacting studies of polymeric chain dimensions and their parametric dependence on molecular weight and excluded volume. In particular, its use for the determination of the weight average molecular weight and the z average radius of gyration has become routine and totally accepted. These routine determinations, however, only utilize a small portion of the available scattering pattern. Much less common is experimental and theoretical work that attempts to use as much of the scattering pattern as can be experimentally determined. Indeed a recent review[3] as well as other research papers imply that there is considerable uncertainty about what new information on chain statistics can be experimentally determined.

Therefore this paper attempts (1) to show more incisively than before what information from the experimentally accessible scattering curve can reasonably be related to the statistical description of the chain from either Monte-Carlo or chain enumeration methods, (2) to interpret newly available light scattering measurements on polystyrene in good and poor solvents to calculate these same chain statistical parameters, and (3) to demonstrate that a better knowledge of the chain statistical parameters is not likely to be obtained unless molecules which are chemically tagged at definite intervals to enhance scattering are used in scattering measurements.

Typical chain dimensions are usually expressed as end-to-end distance or radius of gyration. Over the whole polymer of N segments these distances will be respectively designated r_N and S_N. There is considerable evidence, based on both Monte-Carlo investigations and exact chain enumerations, which shows that r_N^2 and S_N^2, when averaged over all configurations, depend on molecular weight, M, as

M^{γ}, where γ is a constant. This constant is equal to 1 when there are no long-range interactions. In a good solvent, γ is greater than 1 and is frequently given a value of 1.2, which is based on a polymer chain model simulated by a self-avoiding walk on a lattice. In a poor solvent, where only S_N^2 is investigated, γ can be less than 1, although it cannot be less than $\frac{2}{3}$, the value it attains in a "condensed" phase, where the chain is folded into a compact arrangement.

Light scattering measurements are customarily interpreted in terms of sums of r_{ij}^{2p} where r_{ij} is the distance between segments i and j, and $p = 1, 2, \ldots$, averaged over all i and j. Only $\langle S_N^2 \rangle$, the mean squared radius of gyration, is readily determined from routine light scattering measurements so that the parameter γ must be determined by measuring the variation of $\langle S_N^2 \rangle$ with molecular weight on a series of fractions. Only recently[4] have experiments of sufficient precision been made to determine γ by examining a series of polymers having differing molecular weights of well-defined and preferably small polydispersity over a large range of molecular weights. The preparation and characterization of such a series of high molecular weight polymers is tedious and time consuming.

For experimental ease it is desirable to avoid the preparation of such a series of polymers and attempt rather to determine the statistical chain parameters by using only one polymer but using more of the total angular scattering curve. It is shown in this paper that only from the asymptotic expansion of the scattering function can the polydispersity effects be eliminated so that the statistical chain parameters can be determined unambiguously. Practically, this limits the applicability of the method to very high molecular weight polymers analyzed by light scattering or to moderate molecular weight polymers analyzed by low angle X-ray scattering. However, such samples are easily prepared if there is no need to have narrowly dispersed molecular weights. However, it must be emphasized that the statistical parameter that is determined in the above proposed experiment is not the exponent γ that governs the dependence of radius of gyration on molecular weight, but it is another exponent, ν. This exponent ν governs the dependence of $\langle r_{ij}^2 \rangle_N$ on $|i - j|$ assuming that $\langle r_{ij}^2 \rangle_N$ is a function only of the difference of $|i - j|$. This assumption will be discussed later and will be shown to be related to the value of ν, although it may be smaller than the γ actually determined from a series of high molecular weight polymers. It is shown in this paper that reasonable independent theoretical estimates of the value of ν can be made by using the approximate segment correlation function obtained from chain enumeration and Monte-Carlo results. It is finally shown in this paper that experimental values of ν from light scattering measurements on a high molecular sample of polystyrene using the proposed asymptotic expansions are in good agreement with the values deduced from the appropriate chain enumeration and Monte-Carlo calculations.

The light scattering experiments were conducted at several temperatures around the Θ temperature so that it is possible to evaluate ν as a function of temperature near the Θ temperature. The behavior of ν leads to the speculation that this exponent near the Θ temperature behaves in a manner similar to critical region exponents near the critical temperature for other phenomena such as ferromagnetism near the Curie point.

B. Polymer Chain Scattering Function. The polymer chain scattering function is equal to the ratio of the scattered intensity observed at an angle θ to that at zero angle, averaged over all orientations of the molecule. Explicitly, it is denoted as a function of a single variable, μ, where $\mu = (4\pi/\lambda) \sin \theta/2$, and λ is the wavelength of the radiation in the scattering medium.

For a system of flexible randomly oriented macromolecules, Debye[2] derived the following equation for the scattering function $P(\mu)$

$$P(\mu) = \frac{1}{(N+1)^2} \sum_{i,j} \langle \sin(\mu r_{ij})/\mu r_{ij} \rangle \qquad (1)$$

The angle brackets denote that the average is taken over all spatial configurations of the chain molecule. In eq 1, r_{ij} is the distance between scattering elements i and j of the chain, composed of N links ($N + 1$ beads). The scattering function $P(\mu)$ is conveniently expressed as a function of another variable, x, which is related to μ by

$$x = \mu^2 \langle S_N^2 \rangle \qquad (2)$$

$$\langle S_N^2 \rangle = \frac{1}{(N+1)^2} \sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^2 \rangle \qquad (3)$$

The quantity $\langle S_N^2 \rangle$ is also known commonly in polymer science as the mean square radius of gyration of the chain, although it is not related to any particular direction, as defined in mechanics.

Expanding eq 1 in terms of the moments of the vector $\mathbf{r}_{ij}$, one obtains

$$P(\mu) = 1 - \frac{2\mu^2}{3!(N+1)^2} \sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^2 \rangle + \frac{2\mu^4}{5!(N+1)^2} \sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^4 \rangle - \frac{2\mu^6}{7!(N+1)^2} \times \sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^6 \rangle + \ldots \qquad (4)$$

Since

$$x = \frac{\mu^2}{(N+1)^2} \sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^2 \rangle \qquad (5)$$

we have

$$P(\mu) = 1 - \frac{2x}{3!} + \frac{2x^2}{5!}(N+1)^2 \left\{ \frac{\sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^4 \rangle}{\left(\sum_{i=0}^{N} \sum_{j>i}^{N} \langle r_{ij}^2 \rangle \right)^2} \right\} - \frac{2x^3}{7!}(N+1)^4 \left\{ \frac{\sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^6 \rangle}{\left(\sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^2 \rangle \right)^3} \right\} + \ldots \qquad (6)$$

Let $\langle s_N^p \rangle$ be the quantity

$$\langle s_N^p \rangle = \frac{1}{(N+1)^2} \sum_{i=0}^{N-1} \sum_{j>i}^{N} \langle r_{ij}^p \rangle \qquad (7)$$

Obviously, $\langle s_N^2 \rangle = \langle S_N^2 \rangle$, the mean square radius of gyration of the chain. The dimensionless quantities, enclosed by the braces in eq 6, are defined as

$$\Delta_s(2p, 2) = \langle s_N^{2p} \rangle / \langle S_N^2 \rangle^p$$

so that eq 6 can be rewritten as

$$P(\mu) = 1 - \frac{2x}{3!} + \frac{2x^2}{5!}\Delta_s(4, 2) - \frac{2x^3}{7!}\Delta_s(6, 2) + \ldots \qquad (8)$$

For random coils, $\Delta_s(2p,2) = (2p + 1)!/(p + 2)!$, so that eq 8 simplifies to

$$P(\mu) = 1 - \frac{2x}{3!} + \frac{2x^2}{4!} - \frac{2x^3}{5!} + \ldots \qquad (9)$$

Equation 9 can also be obtained when the well-known Debye equation for scattering function for random coils[3]

$$P(\mu) = 2(e^{-x} - 1 + x)/x^2 \tag{10}$$

is expanded in powers of x.

Expansion of $P(\mu)$ in this particular form is convenient for the investigation of the effect of long-range perturbations associated with volume exclusion on the scattering function. This excluded volume effect tends to alter the Gaussian behavior of linear chain molecules. In order to investigate the effect of volume exclusion on the polymer scattering function, the following assumptions are made.

1. The mean square distance between the ith and the jth chain elements is given by the relationship[5]

$$\langle r_{ij}^2\rangle \cong \left(\frac{|i - j|}{N}\right)^{\nu}\langle r_N^2\rangle \tag{11}$$

ν is an arbitrary parameter, whose value depends on the magnitude of the excluded volume effect and which is equal to one in Θ solvent. Thus, $\langle r_{ij}^2\rangle$ is assumed to depend on $|i - j|$ and N only. The fact that $\langle r_{ij}^2\rangle$ depends on N will be indicated by a subscript N outside the angular brackets.

Since $\langle r_N^2\rangle$ varies with N as N^{γ}, eq 11 implies that for $\gamma > \nu$, the value of the average end-to-end distance for a whole molecule of N segments is smaller than the value of the average distance of separation of segments K and $K + N$ in a larger molecule having a total number of segments exceeding $K + N - 1$.

2. Because of the excluded volume effect, the distribution function for the intramolecular distances between i and j elements is not gaussian.[6,7] However, the distribution function $W(\mathbf{r}_{ij})$ is assumed to be spherically symmetric and of the same limiting form for each pair of the segments i and j. Specifically, we assume that

$$W(\mathbf{r}_{ij}) \propto \sigma_{ij}^{-3}F(r_{ij}/\sigma_{ij}) \tag{12}$$

σ_{ij} is the scaling length, which measures the mean separation between segments i and j.

It is assumed that

$$\sigma_{ij} = C\langle r_{ij}^2\rangle_N^{1/2} \tag{13}$$

C, the constant of proportionality, is independent of i, j, and N. It is determined from the calculated second moment of the distribution $W(\mathbf{r}_{ij})$.

Define

$$\langle r_{ij}^p\rangle = \int_0^{\infty} r_{ij}^p W(\mathbf{r}_{ij})4\pi r_{ij}^2 \mathrm{d}r_{ij} \tag{14}$$

Introduce eq 11, 12, and 13 into eq 14. In eq 14, replace $r_{ij}/|i - j|^{\nu/2}$ by a single variable. Since $W(r_{ij})$ is assumed to be of the same form for every pair of segments i and j, and since $C\langle r_N^2\rangle^{1/2}$ is equal to σ_N, the scaling length of the chain-end separation, we obtain

$$\langle r_{ij}^p\rangle = \left(\frac{|i - j|}{N}\right)^{p\nu/2}\langle r_N^p\rangle$$

or (15)

$$\langle r_{ij}^p\rangle = \langle r_{ij}^2\rangle^{p/2}\langle r_N^p\rangle/\langle r_N^2\rangle^{p/2}$$

In eq 7, $\langle r_{ij}^p\rangle$ are replaced by the rhs of eq 15. The summations over i and j are replaced by integrations, and the following equation is derived.

$$P(\mu) = 2\sum_{p=0}^{\infty}(-1)^p\frac{x^p}{(2p + 1)!}\left\{\frac{[(1 + \nu)(2 + \nu)]^p\langle r_N^{2p}\rangle}{(1 + p\nu)(2 + p\nu)\langle r_N^2\rangle^p}\right\} \tag{16}$$

Equation 16 is a useful form for the qualitative investigation of the effect of volume exclusion on the scattering function. Examine first the coefficient of x^p in the summand of eq 16, which is enclosed by braces and denoted by $\Delta_s(2p,2)$

$$P(\mu) = 2\sum_{p=0}^{\infty}\frac{(-1)^p x^p}{(2p + 1)!}\Delta_s(2p, 2) \tag{17}$$

where

$$\Delta_s(2p, 2) = g(p, \nu)\delta_r(2p, 2)$$

$$g(p, \nu) = [(1 + \nu)(2 + \nu)]^p/[(1 + p\nu)(2 + p\nu)]$$

$$\delta_r(2p, 2) = \lim_{N\to\infty}\langle r_N^{2p}\rangle/\langle r_N^2\rangle^p$$

$g(p,\nu)$ depends on volume exclusion, via the exponent ν. For gaussian chains $\nu = 1$. $\delta_r(2p,2)$ is defined as the reduced $2p$th moment of the distribution of chain-end separations. In the absence of long-range interactions of which volume exclusion is a typical case, $\delta_r(2p,2) = \delta_r^0(2p,2) = (2p + 1)!!/3^p$ ($(2p + 1)!! \equiv (2p + 1)(2p - 1)\ldots 1$). On the other hand, both Monte-Carlo computations and exact chain enumeration on self-avoiding walks (chains with volume exclusion effects) show that the distribution of chain ends is definitely nongaussian. Specifically, these computations lead to the following inequality

$$\delta_r(2p, 2) < \delta_r^0(2p, 2)$$

Now introduce another quantity, $\Delta_s^*(2p,2)$, to be defined as follows.

$$\Delta_s^*(2p, 2) = g(p, \nu)\delta_r^0(2p, 2)$$

The chain model for which $\Delta_s(2p,2) = \Delta_s^*(2p,2)$ is based on the assumption that, while $\langle r_{ij}^2\rangle$ is a nonlinear function of $|i - j|$, *the distribution of intramolecular distances is* governed by the gaussian distribution law. This is essentially the chain model employed by Ptitsyn,[8] Loucheux et al.,[9] Hyde,[5] and Peterlin.[10]

The above considerations lead to the following inequality.

$$|\Delta_s(2p, 2) - \Delta_s^0(2p, 2)| \leq |\Delta_s^*(2p, 2) - \Delta_s^0(2p, 2)| \tag{18}$$

$\Delta_s^0(2p,2)$ is the coefficient of $x^p/(2p + 1)!$, eq 16, for gaussian coils

$$\Delta_s^0(2p, 2) = (2p + 1)!/(p + 2)!$$

The implication drawn from the inequalities, eq 18, is that: the assumptions of (1) a nongaussian distribution of the chain-ends separations and of (2) a nonlinear dependence of the second moments of the vector $\mathbf{r}_{ij}$ on $|i - j|$, partially compensate each other in their effects on the computed values of the coefficients in the expansion of $P(\mu)$.

To better illustrate the above arguments, consider the effect of volume exclusion on $\Delta_s(4,2)$, which is the coefficient of $(2/5!)x^2$ in the series expansion of $P(\mu)$ in powers of x. Assume that $\delta_R(4,2) = 1.48$, which is the limiting value for $\langle r_N^4\rangle/\langle r_N^2\rangle^2$ for self-avoiding chains as computed by Monte-Carlo and by chain enumeration methods.[6] For a hypothetical value of $\nu = 1.2$, one obtains $\Delta_s(4,2) = 4.90$ as compared with $\Delta_s^0(4,2) = 5.00$ gaussian coils. On the other hand, it was assumed by previous investigators[8–10] that the distribution of chain links is gaussian, while retaining for ν its value for nonideal chains. (In ref 8–10, a tacit assumption is made that $\langle r_{ij}^2\rangle \simeq |i - j|^{\gamma}$, so that $\nu = \gamma$.) In this case, the deviations of $\Delta_s(4,2)$ from its gaussian coil value of 5 will be *significantly* greater. Thus, taking again $\nu = 1.2$ and $\delta_r^0(4,2) = 5/3$, one obtains $\Delta_s^*(4,2) = 5.52$.

The above considerations provide a qualitative explanation to the observed fact[11–13] that eq 10 (derived for random coils) is of wider applicability than one would expect considering the assumptions upon which its derivation was originally based. More specifically, we provide an explanation of why little distinction can be made between the $P(\mu)$ vs. x curves for polymers in Θ solvents and for polymers in good solvents as long as only low values of x are examined.

McIntyre, Mazur, and Wims[14] and Smith and Carpenter[11] found that x has to exceed the value of 5 before the scattering function $P(\mu)$ for a polymer in a good solvent will show a significant deviation from the scattering function for the same polymers in a Θ solvent.

Since large values of x are required for the purpose of our present investigations, the power expansion of $P(\mu)$ is of little practical use. Instead, an asymptotic expression for $P(\mu)$ that is valid for large values of x is derived. This is done as follows. Equation 1 is rewritten in the following form

$$P(\mu) = \frac{4\pi}{(N+1)^2} \sum_{i,j} \int_0^\infty (\mu r_{ij})^{-1} \times \sin(\mu r_{ij}) r_{ij}^2 W(\mathbf{r}_{ij}) \mathrm{d}r_{ij} \tag{19}$$

Assuming that the distribution function $W(\mathbf{r}_{ij})$ takes on the same functional form for all distances r_{ij}, and is spherically symmetric, then, letting $W(\mathbf{r}_{ij}) = W_{ij}(r)$, eq 19 is rewritten as

$$P(\mu) = 4\pi \int_0^\infty (\mu r)^{-1} \sin(\mu r) r^2 \rho(r) \mathrm{d}r \tag{20}$$

and

$$\rho(r) = \frac{1}{(N+1)^2} \sum_{i=1}^{N} \sum_{j=1}^{N} W_{ij}(r) \tag{21}$$

$\rho(r)\mathrm{d}r$ is the density probability that the distance between two scattering elements, i and j, arbitrarily selected, lies within an interval $(r, r + \mathrm{d}r)$.

Since we assumed that $W(r_{ij})$ is a function of $|i - j|$

$$\rho(r)\mathrm{d}r \cong \int_0^1 (1 - z) W_z(r) \mathrm{d}z \mathrm{d}r \tag{22}$$

where $z = |i - j|/N$.

On the basis of assumptions, eq 11 and 12, $W_z(r)$ is expressed as follows

$$\begin{aligned} W_z(r) &= R_z z^{-3} F(r/R_z) \\ R_z &\cong R_0 z^{\nu/2} \end{aligned} \tag{23}$$

R_0, which is a scaling length of chain-end distance, is proportional to the root mean square of the end-to-end distance in a chain, that is

$$R_0 \propto \langle r_N^2 \rangle^{1/2}$$

In the Appendix it is shown that for commonly employed distributions which fit into the general form given by eq 23[6]

$$\lim_{x \to \infty} P(\mu) = A x^{-1/\nu} - B x^{-2/\nu} \tag{24}$$

where the derivation is restricted to monodisperse systems. The quantities A and B, eq 24, are functions of ν and statistical parameters which describe the shape of the distribution of chain dimensions. For example, if one assumes that this distribution is given by

$$F(y) = D(y) e^{-y^\delta} \qquad y = r/R_z$$

with

$$\lim_{y \to \infty} \log [D(y)] y^{-\delta} = 0 \tag{25}$$

then δ is the designated shape factor. Thus, A and B depend on δ. The polydispersity effects also influence the values of A and B, since N has to be replaced by its average taken over the entire range of degrees of polymerization.[15] In addition, since the radius of gyration of a polydisperse system is defined in such a way that $\lim_{\theta \to 0} [1 - P(\mu)] = x/3$, the variable x, defined by eq 2, will be multiplied by an additional factor equal to

$$\int_0^\infty N^{1+\gamma} f(N) \mathrm{d}N \Big/ \left[\int_0^\infty N f(N) \mathrm{d}N \right]^{1+\gamma}$$

where $f(N)$ is the distribution of the number of statistical links in the polymer chain. Therefore, the coefficient A, derived in the Appendix, for monodisperse systems will include the following additional factor

$$A_{\text{polydisperse}}/A_{\text{monodisperse}} = \left\{ \int_0^\infty N^{1+\gamma} f(N) \mathrm{d}N \right\}^{1/\nu} \times \int_0^\infty N^{1-\gamma/\nu} f(N) \mathrm{d}N \left\{ \int_0^\infty N f(N) \mathrm{d}N \right\}^{-(1+1/\nu)} \tag{26}$$

Similarly, the coefficient B is modified as follows:

$$B_{\text{polydisperse}}/B_{\text{monodisperse}} = \left\{ \int_0^\infty N^{1+\gamma} f(N) \mathrm{d}N \right\}^{2/\nu} \times \int_0^\infty N^{1-2\gamma/\nu} f(N) \mathrm{d}N \left\{ \int_0^\infty N f(N) \mathrm{d}N \right\}^{-(1+2/\nu)} \tag{27}$$

$A_{\text{monodisperse}}$ and $B_{\text{monodisperse}}$ are given by eq A6 and A9, respectively. In Θ solvents, for which $\nu = \gamma = 1$, eq 26 and 27 reduce to

$$A_{\text{polydisperse}}/A_{\text{monodisperse}} = M_z/M_w$$

$$B_{\text{polydisperse}}/B_{\text{monodisperse}} = M_z^2(M_w M_n)$$

Because of polydispersity effects, the coefficients A and B are seen to depend on γ, in addition to ν.

The fact that the exponents of x in eq 24 are functions of ν only can be utilized directly in order to estimate ν. By plotting $\log P(\mu)$ vs. $\log x$ to find the limiting slope at large values of x it is possible to determine ν. This method was discussed earlier by Loucheux, Weill, and Benoit[9] and more recently by Carpenter.[12] We wish to draw attention to the fact that the considerations of these authors are not necessarily restricted to coils with Gaussian distribution. For example, for model chains with distribution functions simulating the non-self-intersecting chain lattice models (volume exclusion), proposed by Mazur[6a] and by Domb, Gillis, and Wilmers,[6b] or for the distribution function proposed by Edwards,[16] the above considerations will also apply.

The major difficulty encountered previously in this kind of analysis of experimental data is the fact that the range of the experimentally determined variable x is insufficient to be used with the limiting equation for $P(\mu)$, that is, with

$$\lim_{x \to \infty} P(\mu) = A x^{-1/\nu} \tag{28}$$

Even in the very best solvent, and at the largest measured angles of scattered radiation, x seldom exceeded the value of 10. To by-pass this difficulty, the second term, which is proportional to $x^{-2/\nu}$, was included in these computations of ν. However, the computation of ν will now depend not only on the dispersity of the polymer solution, but also on the shape of the distribution of intrachain distances. Only on the basis of the light scattering experiments with solutions of very high molecular weight polymers, not available heretofore, one can obtain high enough values of x so that a limiting slope based on eq 28 can be reached within the experimental range of measurements, and ν calculated, without having to consider the effect of the shape of the distribution of chain dimensions on the scattering function.

We presented two equations for $P(\mu)$. The first one, applicable to low values of x, is given by eq 16. The second one, valid only for large x, is given by eq 24. Both these equations incorporate, implicitly, volume exclusion effects. Since, because of volume exclusion, second moment of the vector $\mathbf{r}_{ij}$ is a nonlinear function of $|i - j|$, the parameter ν

has a value that, except for the Θ point, is different from one. In addition, the distribution function $W(\mathbf{r}_{ij})$ is nongaussian. This nongaussianity of $W(\mathbf{r}_{ij})$ affects the values of $\delta_r(2p,2)$, the reduced moments of the chain-end separations, eq 17, and the values of the parameters A and B, eq 24.

As shown above, the investigation of the volume exclusion effects on the chain conformation, performed on the basis of light scattering measurements, can be made only at large values of x. Only then can the parameter ν be isolated and determined independently of the shape of the distribution function and of the polydispersity in the molecular weight distribution. Having determined ν, one can get a qualitative picture of the shape of the distribution $W(\mathbf{r}_{ij})$ from the calculated parameters A and B, eq 24. (For details, see Appendix and ref 17.)

The main purpose of this paper is to evaluate the parameter ν and to find its dependence on temperature and/or solvent. This is done, whenever possible, on the basis of eq 28. Only for polymer solutions in very poor solvent (polystyrene in cyclohexane at 34°), the two-term eq 24 has to be employed, rather than the one-term eq 28.

The derivation of eq 24 and 28 was shown to depend on the following two assumptions: (1) the mean square distances of separations between pairs of segments, $\langle r_{ij}^2\rangle$, are reasonably well approximated by eq 11, and (2) the distribution function for intrachain separations, $W(\mathbf{r}_{ij})$, is given by eq 12. Therefore, the first thing to do is to investigate the approximate validity of the eq 11 and 12. The best procedure to do so is to calculate the moments of the vector $\mathbf{r}_{ij}$, using numerical data obtained by Monte-Carlo and by exact chain enumeration methods.

The remainder of this paper will be divided into two self-containing parts. The first part deals exclusively with the moments of the distribution of intramolecular separations, and is further subdivided into two sections. The first section deals with the second-order moments associated with the distribution of the vector $\mathbf{r}_{ij}$. These moments are expressed in terms of a correlation between any pair of chain elements, using the method of Domb and Hioe.[18] The second section deals with the examination of the validity of eq 12, by computing, using Monte-Carlo method, selected higher order moments of the distribution of intrachain separations.

The second part of this paper deals with the analysis and interpretation of the scattering function of a very high molecular weight polystyrene in good and in poor solvents. The slopes of log $P(\mu)$ vs. log x yield the statistical parameter ν. For polymers in good solvents, this value of ν is compared with the value of ν obtained in section II from Monte-Carlo computations.

II. Moments of the Distribution of the Intramolecular Separations

A. Second Moments of Intramolecular Separations and Their Relations to the Chain Correlation Function. In this section, the following investigations are made.

1. The validity of the approximation

$$\langle r_{ij}^2\rangle_N \cong B_N f|i - j| \tag{29a}$$

where B_N is a proportionality constant, which depends on the chain length only, is examined. This will be tested by computing several second-order moments, which can be related directly to the correlation between any given pair of segments i and j, and for which an explicit knowledge of the distribution of intrachain distances is not needed. These second-order moments are computed, assuming that eq 11 is valid, and are then compared with the same moments that were computed directly by Monte-Carlo and by chain enumeration methods (ref 18 and 19 data calculated with this work).

These second-order moments include mean square distances of separations between fixed pairs of points, a and b, in the chain of N segments. In the present work, a can have one of these values 0, $N/4$, and $N/2$, while b can have one of these values $N/2$, $3N/4$, and N, with $a < b$. Other quantities which can be computed directly from eq 11 are the mean square distances of all polymer segments from a fixed point in the chain. In the present work this fixed point is either identified as the origin of the chain, or as the location of the middle segment. The first of these quantities, commonly designated as $\langle Q_N^2\rangle$, is defined as

$$\langle Q_N^2\rangle = \frac{1}{(N+1)}\sum_{j=1}^{N}\langle r_{0j}^2\rangle_N$$

and is employed in Monte-Carlo computations of the radius of gyration.[20] The other quantity is defined by the relation

$$\langle Q_{N/2}^{\ 2}\rangle_N = \frac{1}{N+1}\sum_{j=1}^{N/2}\langle r_{0j}^2\rangle_N$$

Another quantity, which can be derived directly from eq 11, is the mean square radius of gyration, eq 3.

2. From the list of correlation functions between the ith and the jth chain elements provided in ref 18, select a form which can be further simplified in such a way that it leads to results which are consistent with the assumption, eq 29a.

3. Assign a value to ν, eq 11, which leads to a best numerical agreement between the moments derived from eq 11 and the moments calculated by Monte-Carlo and by chain enumeration methods.

Let $\mathbf{u}_i$ be the bond vector connecting the $(i-1)$th scattering element with the ith scattering element. Each bond vector $\mathbf{u}_i$ is taken to be of a unit length. The vector $\mathbf{r}_N$, which connects the first and the last scattering elements, is given by

$$\mathbf{r}_N = \sum_{i=1}^{N}\mathbf{u}_i$$

Define a correlation $\langle\mathbf{u}_i\cdot\mathbf{u}_j\rangle_N$ between the ith and the jth scattering elements as the scalar product between the bond vectors $\mathbf{u}_i$ and $\mathbf{u}_j$, averaged over all possible configurations of a chain. The mean square distance between the first and the $(N+1)$th scattering elements is given by

$$\langle r_N^2\rangle = N + 2\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle\mathbf{u}_i\cdot\mathbf{u}_j\rangle_N \tag{29b}$$

One can show that, for large N and for fixed values of a and b

$$\frac{\langle r_{ab}^2\rangle}{\langle r_N^2\rangle} = \frac{\int_{a/N}^{b/N}\mathrm{d}x\int_{x}^{b/N}\langle\mathbf{u}_i\cdot\mathbf{u}_j\rangle_N\mathrm{d}y}{\int_{0}^{1}\mathrm{d}x\int_{x}^{1}\langle\mathbf{u}_i\cdot\mathbf{u}_j\rangle_N\mathrm{d}y} \tag{30}$$

$$x = i/N, y = j/N$$

Following Domb and Hioe,[18] assume that $\langle\mathbf{u}_i\cdot\mathbf{u}_j\rangle_N$ can be represented by

$$\langle\mathbf{u}_i\cdot\mathbf{u}_j\rangle_N \cong A\phi(x,y)/N^{2-\gamma} \tag{31}$$

In eq 30, i and j are arbitrarily selected segments between two fixed points a and b.

The exponent γ in eq 31 comes from an established relationship

$$\sum_{i=1}^{N}\sum_{j>1}^{N}\langle \mathbf{u}_i\cdot\mathbf{u}_j\rangle_N = N^{\gamma}$$

(provided that $\gamma > 1$ and N is large enough so that the first term in the rhs of eq 29b can be neglected and therefore, $\langle r_N^2\rangle \propto N^{\gamma}$). $\phi(x,y)$ is singular on $x = y$, and the singularity is of a form $(x - y)^{-2+\gamma}$. Therefore, $\phi(x,y)$ can be formulated as follows:[18]

$$\phi(x,y) = \chi(x,y)/(x - y)^{2-\gamma} \tag{32}$$

In eq 32, $\chi(x,y)$ is a nonsingular function of x and y.

As a first approximation, assume that $\chi(x,y) = B$, a constant. Normalizing $\phi(x,y)$ so that the denominator of eq 30 equals 1, one obtains $B = (\gamma - 1)\gamma$, and therefore

$$\langle r_{ij}^2\rangle_N = \frac{\left(\frac{|i - j|}{N}\right)^{\gamma}}{(\gamma - 1)\gamma}\,(\gamma - 1)\gamma\langle r_N^2\rangle = C|i - j|^{\gamma} \tag{33}$$

C is a numerical constant, which is independent of N. For $\gamma = 6/5$, $B = 0.24$.

We know that eq 33 leads to incorrect results. From eq 33 we would obtain that

$$\begin{aligned}\langle S_N^2\rangle/\langle r_N^2\rangle &= [(1 + \gamma)(2 + \gamma)]^{-1}\\ \langle Q_N^2\rangle/\langle r_N^2\rangle &= (1 + \gamma)^{-1}\end{aligned} \tag{34}$$

Taking again $\gamma = 6/5$, the results are shown to be at variance with Monte-Carlo computations and with the exact chain enumeration. (See Table I, compare columns 2 and 3.)

In order to get the second moments of the chain correlation function to agree as closely as possible with the same moments, computed directly by either chain enumeration or by Monte-Carlo computations, Domb and Hioe[18] suggested several alternative forms for the function $\chi(x,y)$. These functions are restricted to expansions in power series in $x - y$ and in $1 - (x + y)$, retaining up to quadratic terms of these variables. Of the three forms for $\chi(x,y)$ proposed in ref 18, we selected the particular form in which the contributions of terms involving $1 - (x + y)$ are the smallest. The function for $\chi(x,y)$ selected after terms involving $(i + j)$ have been deleted is the following one:

$$\chi(x,y) = B[1 - (x - y)]^2 \tag{35}$$

In eq 35, the normalization constant B is found to be

$$B = \left[\frac{1}{(\gamma - 1)\gamma} - \frac{2}{\gamma(\gamma + 1)} + \frac{1}{(\gamma + 1)(\gamma + 2)}\right]^{-1} \tag{36}$$

Assuming $\gamma = 6/5$, one obtains $B = 0.282$. In the full form for $\chi(x,y)$ (eq 29c, ref 18), $B = 0.295$. There is a close agreement between the approximate value of B (assuming that $\chi = \chi(|i - j|/N)$ only) and the more accurate value of B, given in ref 18. The slight difference between these two quantities is attributed to the omission of terms involving $i + j$ from eq 35.

From eq 31, 32, and 33 and the assumption that $\gamma = 1.2$, eq 37 is found. This equation for $\langle r_{ij}^2\rangle/\langle r_N^2\rangle$ serves as a

$$\frac{\langle r_{ij}^2\rangle_N}{\langle r_N^2\rangle} = 0.282\left\{4.17\left(\frac{|i - j|}{N}\right)^{1.2} - 0.758\left(\frac{|i - j|}{N}\right)^{2.2} + 0.143\left(\frac{|i - j|}{N}\right)^{3.2}\right\} \tag{37}$$

good approximation that is valid for the two extreme cases of interest, namely when $|i - j| \gg 1$ and when $|i - j|/N \ll 1$. In the limit of $i = 0$ and $j = N$, $\langle r_{ij}^2\rangle_N = \langle r_N^2\rangle$, as expected. For $|i - j| \ll N$, we obtain

$$\frac{\langle r_{ij}^2\rangle_N}{\langle r_N^2\rangle} = 1.17\left(\frac{|i - j|}{N}\right)^{1.2}$$

which is reasonable.

The following relationships of $\langle S_N^2\rangle$ and $\langle O_N^2\rangle$ to $\langle \mathbf{u}_i\cdot\mathbf{u}_j\rangle_N$ in terms of reduced variables, $x = i/N$ and $y = j/N$, can be derived:

$$\langle S_N^2\rangle = N^2\int_0^1 \mathrm{d}x\int_x^1 (1 - y)x\langle \mathbf{u}_i\cdot\mathbf{u}_j\rangle_N \mathrm{d}y \tag{38}$$

and

$$\langle Q_N^2\rangle = N^2\int_0^1 \mathrm{d}x\int_x^1 (1 - y)\langle \mathbf{u}_i\cdot\mathbf{u}_j\rangle_N \mathrm{d}y \tag{39}$$

Substituting for $\langle \mathbf{u}_i\cdot\mathbf{u}_j\rangle_N$ in eq 38 and 39 using eq 31, 32, and 35 and then integrating gives

$$\frac{\langle S_N^2\rangle}{\langle r_N^2\rangle} = \frac{1}{6}\left[1 - 2\frac{(\gamma - 1)}{3 + \gamma} + \frac{\gamma(\gamma - 1)}{(3 + \gamma)(4 + \gamma)}\right] \tag{40}$$

and

$$\frac{\langle Q_N^2\rangle}{\langle r_N^2\rangle} = \frac{1}{6}\left[2 + \gamma - 2(\gamma - 1) + \frac{\gamma(\gamma - 1)}{3 + \gamma}\right] \tag{41}$$

For $\gamma = 1$, $\langle S_N^2\rangle = \langle r_N^2\rangle/6$, $\langle O_N^2\rangle = \langle r_N^2\rangle/2$, as expected. For $\gamma = 6/5$, $\langle S_N^2\rangle = 0.153\langle r_N^2\rangle$ which is remarkably close to the exact result of $0.157\langle r_N^2\rangle$ obtained from Monte-Carlo computations.[20]

The three-term expressions for the $\langle r_{ij}^2\rangle_N$, $\langle S_N^2\rangle$, and $\langle Q_N^2\rangle$ are derived under the assumption that the correlations between the ith and the jth chain elements are functions of $|i - j|$ only; they are nevertheless cumbersome and unwieldy, particularly when they are used for derivation of higher order moments. Consequently, a simpler, one-term formula for $\langle r_{ij}^2\rangle_N$ will be used for further calculations. While the simpler formula will not hold for small values of $|i - j|$, the contributions of the small intramolecular separations toward the radius of gyration and toward higher moments of the averaged intramolecular separations were earlier shown to be negligible,[3] when N is sufficiently large. The following simple formula is chosen to replace eq 37 for $\langle r_{ij}^2\rangle_N$:

$$\langle r_{ij}^2\rangle_N = \left(\frac{|i - j|}{N}\right)^{\nu}\langle r_N^2\rangle \tag{42}$$

With this simplification

$$\langle S_N^2\rangle = \langle r_N^2\rangle/(1 + \nu)(2 + \nu) \tag{43}$$

and

$$\langle Q_N^2\rangle = \langle r_N^2\rangle/(1 + \nu) \tag{44}$$

To find the best value for ν, the right-hand sides of eq 43 and 44 are equated to the values of these quantities, calculated from eq 40 and 41, with $\gamma = 1.2$, as follows: (1) $[(1 + \nu)(2 + \nu)]^{-1} = 0.153$ and (2) $(1 + \nu)^{-1} = 0.471$. From (1) $\nu = 1.105$ and from (2) $\nu = 1.096$. An intermediate value of $\nu = 1.10$ was chosen for further calculations. As a final check, Table I includes all the second moments which can be directly evaluated from the known correlation function $\phi(x,y)$ and for which exact numerical data are available in the literature. These exact moments are compared first with the crude assumption that $\langle r_{ij}^2\rangle_N \simeq |i - j|^{\gamma}$, that is, that the mean square separation between two chain elements i and j in a chain of N links is independent of N and second, comparison is made on the assumption that $\langle r_{ij}^2\rangle_N$ depends also on N, as postulated by our compromise formula, eq 42, with $\nu = 1.10$.

It is clear from Table I that the value of $\nu = 1.1$ agrees well with the computed second moments of the correlation function $\langle \mathbf{u}_i\cdot\mathbf{u}_j\rangle_N$ and is superior to the assumption that ν

Table I
Estimates for Various Reduced Second Moments, Nonself-Intersecting Chain, Cubic Lattice

Moment	Computed	Assumption	
		$\nu = \gamma = 1.2$	$\nu = 1.1$
$\langle r_{0,N/4}{}^2\rangle_N/\langle r_N{}^2\rangle$	0.2047 ± 0.0050^a	0.189	0.218
$\langle r_{N/4,N/2}\rangle_N/\langle r_N{}^2\rangle$	0.2203 ± 0.005^a		
$\langle r_{0,N/2}{}^2\rangle_N/\langle r_N{}^2\rangle$	$0.4607 \pm 0.0094,^a$ $0.460 + 0.005^b$	0.435	0.466
$\langle r_{N/4,3N/4}{}^2\rangle_N\langle r_N{}^2\rangle$	$0.4893 \pm 0.0168,^a$ 0.495 ± 0.005^b		
$\langle r_{0,3N/4}{}^2\rangle_N\langle r_N{}^2\rangle$	0.737 ± 0.0137^a	0.708	0.729
$\langle Q_N{}^2\rangle/\langle r_N{}^2\rangle$	$0.472 \pm 0.002,^a$ 0.476 ± 0.001^c	0.454	0.476
$\frac{1}{N+1}\sum_{j=0}^{N}\langle r_{j,N/2}{}^2\rangle/\langle r_N{}^2\rangle$	0.222 ± 0.003^b	0.198	0.222
$\langle S_N{}^2\rangle/\langle r_N{}^2\rangle$	$0.155 \pm 0.001,^a$ 0.158 ± 0.001^c	0.142	0.154

[a] Data from ref 18 and 19. [b] Data calculated with this work. [c] Data from ref 20.

$= \gamma = 1.2$ (which represents the case when the function $\chi(x,y)$ is a constant).

These arguments also demonstrate that the selected value of 1.10 for the exponent ν is a direct consequence of the assumption that $\gamma = 1.2$ and that the correlation function between any pair of segments may be approximated by 31, 32, and 35. Therefore, the value $\nu = 1.10$ is consistent with both $\gamma = \frac{6}{5}$ and with an assumption that $\chi(x,y) = B[1 - (x - y)]^2$. $\chi(x,y)$ is, in turn, related to the correlation function $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle_N$ through

$$\chi(x,y) \propto [N(x - y)]^{2-\gamma}\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_N = |i - j|^{2-\gamma}\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_N \tag{45}$$

Equations 42–44 can be derived directly, by assuming that the correlation function between segments i and j is approximated as follows

$$\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_N \cong \nu(\nu - 1)|i - j|^{\nu-2} \tag{46}$$

or, by using eq 32, as

$$\phi(x,y) = \nu(\nu - 1)|y - x|^{\nu-2}$$
$$x = i/N, \quad y = j/N$$

Because of the approximations involved eq 46 can be employed only for the computations of moments in their reduced forms, and only for cases when the contributions of small values of $|i - j|$ toward the computed averages can be neglected.

B. Evaluation of Higher Order Reduced Moments and Their Verification from Monte-Carlo Computations. Higher order reduced averaged moments of the general form

$$\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^p\rangle\Big/\left(\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^2\rangle\right)^{p/2}$$

have to be evaluated for light scattering calculations concerning polymers.

In order to obtain fourth-order moments, such as

$$\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^4\rangle$$

and

$$\sum_{j=1}^{N}\langle r_{0j}{}^4\rangle$$

a correlation function involving four chain elements

$$\langle(\mathbf{u}_i \cdot \mathbf{u}_j) \cdot (\mathbf{u}_k \cdot \mathbf{u}_l)\rangle_N$$

is needed. Rather than proceeding along these lines of establishing higher order correlations, we will adopt a different approach, that does not involve correlation function between segments. We start with the assumption that eq 12 describes correctly the general shape of the distribution function $W(\mathbf{r}_{ij})$. The second moment of this distribution, $\langle r_{ij}{}^2\rangle_N$, is assumed to be given by eq 11. Moreover, the reduced moments of order p of the chain-end distribution, $\delta_R(p,2) \equiv \langle r_N{}^p\rangle/\langle r_N{}^2\rangle^{p/2}$, are assumed to be known from the available data based on Monte-Carlo computations on self-avoiding walks in a lattice.

From (11), (12), and (14) the following equations are derived:

$$\langle r_{ij}{}^p\rangle_N = C^3\int_0^\infty \frac{r^p}{\left(\frac{|i-j|}{N}\right)^{3\nu/2}\langle r_N{}^2\rangle^{3/2}} \times F\left(\frac{Cr}{\left(\frac{|i-j|}{N}\right)^{\nu/2}\langle r_N{}^2\rangle^{1/2}}\right) 4\pi r^2 \mathrm{d}r = \left(\frac{|i-j|}{N}\right)^{p\nu/2}\langle r_N{}^p\rangle = \left(\frac{|i-j|}{N}\right)^{p\nu/2}\delta_R(p,2)\,\langle r_N{}^2\rangle^{p/2} \tag{47}$$

$$\frac{1}{(N+1)}\sum_{j=1}^{N}\langle r_{0j}{}^p\rangle = C^3\int_0^\infty \mathrm{d}r\int_0^1 \frac{r^p}{x^{3\nu/2}\langle r_N{}^2\rangle^{3/2}} F\left(\frac{Cr}{x^{\nu/2}\langle r_N{}^2\rangle^{1/2}}\right) 4\pi r^2 \mathrm{d}x = \frac{1}{(p/2)\nu + 1}\langle r_N{}^p\rangle = \frac{\delta_R(p,2)}{(p/2)\nu + 1}\langle r_N{}^2\rangle^{p/2} \tag{48}$$

$$\frac{1}{(N+1)^2}\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^p\rangle = \frac{4\pi C^3}{\langle r_N{}^2\rangle^{3/2}}\int_0^\infty r^{2+p}\mathrm{d}r\int_0^1 \mathrm{d}x\int_x^1 (y - x)^{-3\nu/2} \times F\left(\frac{Cr}{(y - x)^{\nu/2}\langle r_N{}^2\rangle^{1/2}}\right)\mathrm{d}y = \langle r_N{}^p\rangle\int_0^1 \mathrm{d}x \times \int_x^1 (y - x)^{p\nu/2}\mathrm{d}y = \frac{\langle r_N{}^p\rangle}{((p/2)\nu + 1)((p/2)\nu + 2)} = \frac{\delta_R(p,2)}{((p/2)\nu + 1)((p/2)\nu + 2)}\langle r_N{}^2\rangle^{p/2} \tag{49}$$

In eq 48 and 49 $x = i/N$ and $y = j/N$.

The constant C which appears in eq 47–49 is independent of i, j, and N. It depends on the parameters which describe the shape of the distribution function. This constant is determined from the computed second moments of $W(\mathbf{r}_{ij})$.

In eq 47–49, $\gamma_R(p,2)$ are the reduced moments of the distribution functions of the chain-end separation, defined by $\langle r_N{}^p\rangle/\langle r_N{}^2\rangle^{p/2}$.

The validity of eq 47–49 was checked by computing some of the reduced higher moments, using the Monte-Carlo technique. The computed reduced moments are extrapolat-

Table II

	Computed Monte-Carlo	Eq 47		Gaussian distribution		Gaussian coil
		$\nu = 1.1$	$\nu = \gamma = 1.2$	$\nu = 1.1$	$\nu = \gamma = 1.2$	
$\langle r_{N/4,3N/4}{}^4\rangle_N/\langle r_N{}^2\rangle^2$	0.335 ± 0.002	0.322	0.280	0.363	0.316	0.417
$\langle r_{0,N/2}{}^4\rangle_N/\langle r_N{}^2\rangle^2$	0.304 ± 0.002					
$\langle r_{N/4,3N/4}{}^6\rangle_N/\langle r_N{}^2\rangle^3$	0.286 ± 0.004	0.287	0.233	0.395	0.321	0.486
$\langle r_{0,N/2}{}^6\rangle_N/\langle r_N{}^2\rangle^3$	0.252 ± 0.003					

Table III

Moments	Computed Monte-Carlo	$\nu = 1.1$	$\nu = \gamma = 1.2$	Gaussian distribution $\nu = 1.1$	Gaussian distribution $\nu = \gamma = 1.2$	Gaussian coil
$\frac{1}{N+1}\sum_{j=0}^{N}\langle r_{j,N/2}{}^4\rangle_N/\langle r_N{}^2\rangle^2$	0.0954 ± 0.0007	0.1006	0.0824	0.1134	0.0929	0.1389
$\frac{1}{N+1}\sum_{j=1}^{N}\langle r_{0j}{}^4\rangle_N/\langle r_N{}^2\rangle^2$	0.4552 ± 0.0035	0.462	0.435	0.521	0.490	0.556
$\frac{1}{(N+1)^2}\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^4\rangle_N/\langle r_N{}^2\rangle^2$	0.1114 ± 0.0007	0.110	0.0989	0.124	0.111	0.139
$\frac{1}{N+1}\sum_{j=0}^{N}\langle r_{j,N/2}{}^6\rangle_N/\langle r_N{}^2\rangle^3$	0.0583 ± 0.0007	0.0667	0.0506	0.0919	0.0858	0.1215
$\frac{1}{N+1}\sum_{j=1}^{N}\langle r_{0j}{}^6\rangle_N/\langle r_N{}^2\rangle^3$	0.637 ± 0.007	0.657	0.614	0.904	0.845	0.972
$\frac{1}{(N+1)^2}\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^6\rangle_N/\langle r_N{}^2\rangle^3$	0.121 ± 0.001	0.124	0.110	0.171	0.151	0.194
$\frac{1}{(N+1)^2}\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^4\rangle/\langle S_N{}^2\rangle^2$	4.636 ± 0.001	4.662	4.90	5.256	5.501	5.00
$\frac{1}{(N+1)^2}\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^6\rangle/\langle S_N{}^2\rangle^3$	32.49 ± 0.05	34.21	38.38	47.19	52.69	42.00

ed to infinite chain lengths, and the values so obtained are compared with the values found from the relationships shown above. The following quantities were computed:

$$\langle r_{0,N/2}{}^4\rangle_N,\ \langle r_{N/4,3N/4}{}^4\rangle_N,\ \langle r_{0,N/2}{}^6\rangle_N,\ \langle r_{N/4,3N/4}{}^6\rangle_N,$$
$$(N+1)^{-1}\sum_{j=1}^{N}\langle r_{0j}{}^4\rangle,\ (N+1)^{-1}\sum_{j=0}^{N}\langle r_{j,N/2}{}^4\rangle,$$
$$(N+1)^{-2}\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^4\rangle,\ (N+1)^{-1}\sum_{j=1}^{N}\langle r_{0j}{}^6\rangle,$$
$$(N+1)^{-1}\sum_{j=0}^{N}\langle r_{j,N/2}{}^6\rangle,\ (N+1)^{-2}\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^6\rangle$$

Some of these quantities involve intrachain dimensions of subchains with the same number of intervening elements. Two extreme cases were evaluated: (1) intrachain distances of half-chains, centered symmetrically about the middle element of a chain, and (2) intrachain distances of half-chains originating from one of the two chain ends. These computations were performed in order to check the magnitude of the error made in the assumption that the location of the sequence $|i-j|$ does not significantly affect the computed averages.

Table II presents the fourth and sixth reduced moments for distances between pairs of segments separated by $N/2$ chain elements, in a chain of N elements for the two extreme cases. The computed results refer to chains of infinite length. These results were obtained by extrapolation of data computed for non-self-intersecting chains on a cubic lattice with up to 80 segments, at 10-step intervals.

The numerical data, in their reduced form, were fitted into a polynomial in inverse powers of N, using the least-square method. Polynomials of first, second, and third degrees were tried. The polynomial selected as the best fit for the data was determined as having the smallest residual standard deviation. The extrapolated reduced moments are then given by the constant term of the chosen polynomial. The possible range in the extrapolated data is given by the standard deviation of the constant term. The same procedure was employed with the data of Table I, footnote *b*, and with the data of Table III. A total of 32,000 chains was generated.

The reduced second moments (included in Table I, together with results from ref 18 and 19) were found to reach their limiting values so rapidly that extrapolation to infinite chain length was hardly needed. However, the convergence to the limiting values becomes slower, as higher order reduced moments are computed. Thus, no effort was made to go beyond the sixth moments. In addition to the computed results, column 3 of Table II shows the results based on eq 47, with $\nu = 1.1$. For the reduced chain-end moments, $\delta_R(p,2)$, data from ref 6a were used. Thus, in all the computations, it was assumed that $\delta_R(4,2) = 1.479$ and $\delta_R(6,2) = 2.824$. The data presented in column 4 were computed from eq 47, but with the assumption that $\nu = \gamma = 1.2$. In columns 5 and 6, gaussian-chain values were used for the reduced chain-end moments. Thus, values of $\delta_R{}^0(4,2) = 5/3$ and $\delta_R{}^0(6,2) = 35/9$ were employed in these columns. Finally, in column 7, the random coil model was used, that is, $\nu = 1$ and $\delta_R(p,2) = \delta_R{}^0(p,2)$. It is evident from Table II that the assignment of $\nu = 1.1$, combined with the values for the reduced moments of mean squares end-to-end distances of separation computed for self-avoiding chains (ref 5 and 6a), leads to the best agreement with the Monte-Carlo computations. The results based on the random coil model differ markedly from the Monte-Carlo results.

In Table III, calculations similar to those in Table II are presented for

$$(N+1)^{-1}\frac{\sum_{j=1}^{N}\langle r_{0j}{}^p\rangle}{\langle r_N{}^2\rangle},\quad (N+1)^{-1}\frac{\sum_{j=0}^{N}\langle r_{j,\,N/2}{}^p\rangle}{\langle r_N{}^2\rangle^{p/2}},$$

$$(N+1)^{-2}\frac{\sum_{j=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^p\rangle}{\langle r_N{}^2\rangle^{p/2}}$$

Two values for p were assumed: $p = 4$ and $p = 6$. Again, the same conclusion can be drawn, namely that the assumption that $\nu = 1.1$, together with the values for the reduced moments of chain-end separation, $\delta_R(p,2)$ given in ref 6, leads to the best agreement with the Monte-Carlo computations, presented in column 1. In the last two lines of Table III, the quantities

$$\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^p\rangle$$

are reduced by $\langle S_N{}^2\rangle^{p/2}$, rather than by $\langle r_N{}^2\rangle^{p/2}$. Those reduced moments are identical with the reduced moments symbolized by $\Delta_s(2p,2)$, eq 8. $\Delta_s(2p,2)$ are the coefficients of $[(-1)^p 2/(2p+1)!]\ x^p$ in the expansion of the $P(\mu)$ by power series in x, eq 17.

Of some interest is the comparison of the last three columns of Table III with the Monte-Carlo data, column 1. Consider first the reduced moments of the form

$$\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^p\rangle/\langle r_N{}^2\rangle^{p/2}$$

computed for two hypothetical chain models: (1) for gaussian coil model (column 6, Table III), and (2) for the model with $\nu > 1$ and with a gaussian distribution of chain-end separations (columns 4 and 5). When these moments are compared with the corresponding Monte-Carlo computed reduced moments (column 1), it is seen that the second chain model leads to better agreement with the Monte-Carlo computations than does the first chain model. Now, consider the reduced moments of the form

$$\sum_{i=0}^{N-1}\sum_{j>i}^{N}\langle r_{ij}{}^p\rangle/\langle S_N{}^2\rangle^{p/2} \equiv \Delta_s(p,2)$$

and make the same comparison as before. This time it is seen that the Monte-Carlo computed reduced moments agree better with the moments computed for the gaussian chain model than with the second chain model. This point was already discussed in the Introduction to this paper (see discussion following eq 17). Comparison of columns 2–6, Table III, points to the fact that an increase in ν tends to increase $\Delta_s(p,2)$. On the other hand, the effect of volume exclusion on the distribution of chain-end separations tends to decrease $\Delta_s(p,2)$. For the specific value of $\nu = 1.1$, the over-all effect of volume exclusion on $\Delta_s(p,2)$ is to reduce this quantity as compared with $\Delta_s{}^0(p,2)$ (see eq 18).

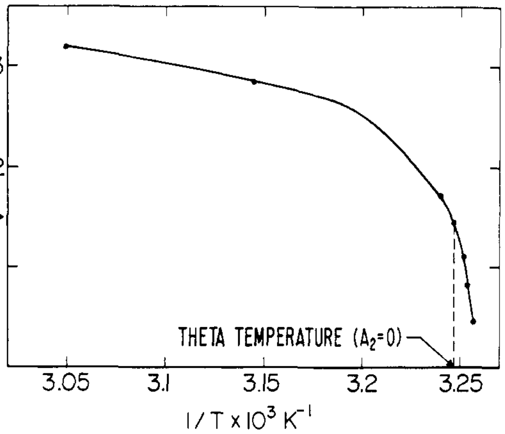

Figure 1. Mean squared radius of gyration (arbitrary scale) vs. $1/T \times 10^3 \mathrm{K}^{-1}$ for polystyrene ($M_w \simeq 4.4.10^7$) in cyclohexane, from light scattering data. Θ temperature is indicated by A_2, the second virial coefficient, equal to 0. Basic data used in the determination of $\langle S^2\rangle$ are taken from ref 4.

III. Light Scattering Studies of Very High Molecular Weight Polystyrene

Polystyrene samples of very high molecular weight were synthesized by McIntyre et al. using anionic polymerization.[21] The weight average and z average molecular weight were determined by Slagowski et al. from sedimentation equilibrium experiments.[22] The highest molecular weight polystyrene sample was found by these authors to have a M_w of 4.37×10^7 and a M_z/M_w ratio of 1.11. Systematic light scattering experiments were performed by Slagowski over a large angular range (15–135°) and over a large range of temperatures in cyclohexane (34, 34.5, 35, 35.4, 36.4, 45, and 55°).[4] From phase equilibrium experiments and virial coefficient measurements, 35.5° was chosen to be the Θ temperature for this solvent. Below 35° the solvent is a very "poor" solvent (second virial coefficient is -17×10^{-5} cm^3 mol/g^2), but it is not a phase-separated liquid, nor does the solution exhibit critical opalescence. At 55° the solvent is moderately good as indicated by its second virial coefficient of 3.4×10^{-5} cm^3 mol/g^2. Also, the same sample was measured by Slagowski in benzene at 40°.[4] The second virial coefficient is 18×10^{-5} cm^3 mol/g^2. Thus, the second virial coefficient in the best available solvent (benzene) has almost become of equal magnitude to the one in poorest solvent (cyclohexane at 34°), but of opposite sign. Over the temperature range in cyclohexane (34 to 55°), the size of the molecule as measured by its radius of gyration has increased threefold. The best available solvent (benzene) would only increase the molecular size by an additional factor of 1.4 and the second virial coefficient by a factor of $\simeq 5$.

The absolute molecular weights were determined independently by the equilibrium ultracentrifuge. Light scattering data were analyzed from typical Zimm plots[15] in such a way that the intercepts in these plots were fixed to the ultracentrifuge-determined molecular weight. Thus, the initial slope is drawn from these plots and a reasonable estimate of the mean square radius of gyration might be obtained. (Even if such experimental precaution had not been taken, the uncertainty in x would not exceed $\simeq 10\%$ and any numerical values of ν would not be seriously affected.) In Figure 1, the mean square radius of gyration (in arbitrary scale) for polystyrene in cyclohexane is plotted vs. $1/T$, the reciprocal absolute temperature. Θ temperature is indicated as a temperature at which the second virial coefficient is zero. The sudden contraction of the chain in the

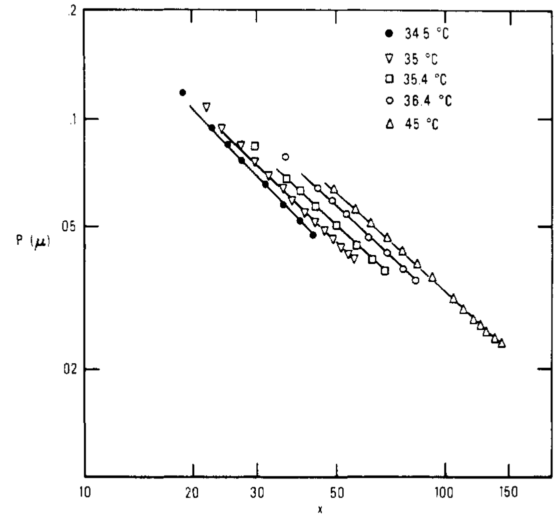

Figure 2. $P(\mu)$ as a function of x on double logarithmic scale. Data are for polystyrene (M_w = 44 × 10^6) in cyclohexane at 34.5, 35, 35.4, 36.4, and 45°. Original data are taken from ref 4.

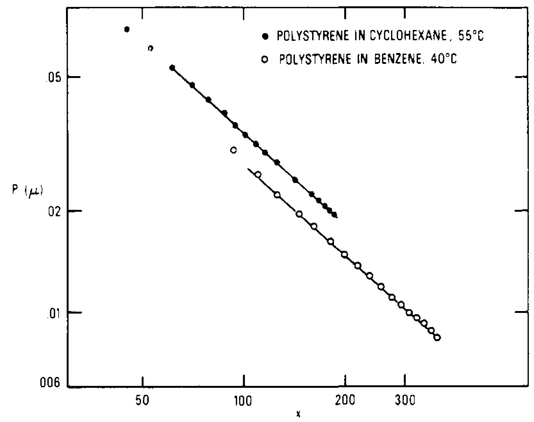

Figure 3. $P(\mu)$ as a function of x on double logarithmic scale. Data are for polystyrene (M_w = 44 × 10^6) in cyclohexane at 55° and in benzene at 40°. Original data are taken from ref 4.

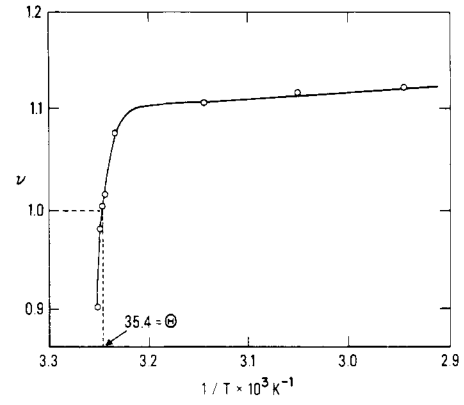

Figure 4. ν vs. $1/T$ for polystyrene cyclohexane system. M_w = 44 × 10^6 (data taken from asymptotes of light scattering curves).

Table IV
The Constants ν and A, Eq 28, Obtained from Experimental Data[a]

T, °C	ν	A
	Cyclohexane	
34.5	0.901	3.03
35	0.979	2.43
35.4	1.012	2.32
36.4	1.074	2.20
45	1.101	2.17
55	1.115	2.13
	Benzene at 40°	
	1.102	1.84

[a] Polystyrene in cyclohexane and benzene. M_w = 4.27 × 10^7, M_z/M_w = 1.11.

vicinity of Θ temperature is evident. The experimental data employed in Figure 1 are taken from ref 4. With the exception of polystyrene in cyclohexane at 34°, the asymptotic behavior of the scattering function had been achieved since the log–log plots of $P(\mu)$ vs. x were found to approach limiting straight lines for large values of x. These plots are shown in Figures 2 and 3. In these figures, only results for large values of x are shown. Data were taken from ref 4. The data were analyzed for a fit by eq 28 using the least-square method, except for data for 34°, which are discussed later. Care was taken that the deviations of the given values of log $P(\mu)$ from the calculated values be random. If the deviations show systematic behavior (that is, they are not random) the lowest value of x employed in the least-square fitting of experimental data was increased. This process is repeated until the deviations appear to be random. In Table IV we group ν and A, calculated by the least-square fitting of the log $P(\mu)$ vs. log x data, according to eq 28 for cyclohexane at all temperatures except 34°.

As is evident from Table IV, the largest value of ν, obtained under experimental conditions described above, is about 1.12, in close agreement with the predicted value of 1.1, based on our theoretical model. In Figure 4, ν is plotted vs. $1/T$. From this plot we identify the Θ temperature as 35.4°, which is very slightly different from the temperature at which the second virial coefficient is found to be zero (T = 35.5°).

We also calculated ν from the scattering data of polystyrene in benzene at 40° and for polystyrene in cyclohexane at 34°. Due to much smaller scattering intensities, the data for $P(\mu)$ in benzene, particularly at large scattering angles, are less accurate than the data for polystyrene in cyclohexane. This reflects itself in a rather large standard deviation of the fit (0.025 as compared to 0.01 for the polystyrene–cyclohexane system). The results obtained for two different molecular weight samples are ν = 1.10 and 1.06.

For polystyrene in cyclohexane at 34°, the highest calculated value of x, corresponding to the scattering angle of 135°, was found to be equal to 22. This fact precludes us from using the limiting one-term equation for $P(\mu)$, eq 28. Instead, eq 24 was employed. The best fit of ν, A, and B was found by varying $1/\nu$ at constant interval, and calculating, using least-square analysis, values of A and B together with the residual standard deviation of the fit of eq 24. Theoretically, the set of ν, A, and B, for which the standard deviation is the smallest, represents the best fit of eq 24 to the experimental data. However, as is seen from Table V, the standard deviation changes but slightly with the change in ν, and the set of values of ν, A, and B, for which this residual standard deviation is minimum, does not necessarily represent the best values of these parameters. We will therefore be satisfied with the approximate upper bound for ν. This bound is found from the following considerations. For unrestricted chain, the ratio B/A is nothing less than the ratio of z average molecular weight average to number average molecular weight, that is, $B/A = M_z/M_n$. Thus, $B/A > 1$. Since $M_z/M_w = 1.11$ and $M_w > M_n$, $(B/A)_0$

Table V
Least-Squares Data for Polystyrene in Cyclohexane (34°)

ν	A	B	Res stand dev
0.862	2.07	−1.97	0.003155
0.847	2.22	−1.45	0.003120
0.833	2.37	−0.833	0.003086
0.820	2.53	−0.106	0.003054
0.806	2.71	0.744	0.003025
0.794	2.89	1.73	0.003001
0.781	3.08	2.88	0.002982
0.769	3.28	4.19	0.002970
0.758	3.49	5.70	0.002967
0.746	3.72	7.11	0.002974
0.735	3.95	9.40	0.002992

> 1.11. Inspection of the eq A6 and A9 points to the following.

For polymer in good solvent (i.e., $\nu > 1$ and $\delta > 2$), (A/B)(monodisperse) > 1, while for poor solvents, ($\nu < 1$ and $\delta \leq 2$), (B/A)(monodisperse) > 1. At Θ point, $A_{\text{monodisperse}} = B_{\text{monodisperse}} = 2$. Assuming, to a first approximation, that (B/A)(polydisperse) $=$ (B/A)(monodisperse)(M_z/M_n); it follows that, below Θ point, $B/A > 1.11$. Inspection of Table V reveals that this inequality is satisfied for $\nu \leq 0.78$. The minimum standard deviation of the fit happens to correspond to $\nu = 0.76$. Thus, we surmise that $\nu < 0.78$. This remarkably low limit on ν, at a temperature which is only 1.5° lower than the Θ temperature, tends to confirm our conjecture that the chain undergoes rapid conformational transition in the neighborhood of the Θ temperature.

The coefficient A calculated from the scattering data of polystyrene in benzene at 40° is considerably smaller than the one for polystyrene–cyclohexane at 55°. Since both solutions are of the same molecular weight, and since ν is practically the same, we surmise that the shape of the distribution of intramolecular separations is different in those two systems. Basing ourselves on the distribution employed in the Appendix, which is characterized by a single decay parameter δ, we conclude that δ is greater (the decay of the distribution of large intramolecular separations is more rapid) in benzene than in cyclohexane. This is to be expected, since the polystyrene–benzene system comprises what the polymer scientists call a "very good solvent" as evidenced from the high value of the second virial coefficient. It is postulated that, as the volume exclusion effects become more pronounced, the value of the shape factor δ will increase.[6a,23] And indeed, approximate calculation of δ from eq A6, corrected for polydispersity effects according to the method of Zimm and Schultz, indicates that δ is around 2.5 for the polystyrene–benzene solution and close to 2 for the polystyrene–cyclohexane solution.

The experiments thus agree with the theoretical calculations to the effect that ν is smaller than γ. Also the value for ν ($\nu = 1.10$) obtained from calculations based on a lattice-simulated chain model with volume exclusion effects agrees well with ν as determined from light scattering data for polystyrene in cyclohexane at $T = 55°$ and in benzene at 40°.

Another more striking conclusion about chain behavior can be made if the temperature dependence of ν is considered. According to Figure 4, ν is practically constant for $T > T_\Theta$ and it drops rapidly around the Θ temperature to a value which is considerably smaller than one. This behavior of ν as a function of temperature tends to confirm a conjecture made previously by a number of researchers, that a single polymer chain undergoes a first-order transition at a certain critical point.[24-26] At this point the chain abandons its coil-like conformation and it assumes a more compact configuration. This conjecture can be heuristically justified, as follows. A self-avoiding walk can be considered to be a ferromagnet with zero degrees of freedom for spin interactions, as suggested by deGennes,[27] in which case the exponent γ and the "effective" exponent ν belong to a group of critical indices. Using the smoothness postulate of Griffiths,[28] these exponents should remain constant down to the transition point. Thus, in Figure 4, ν could be equal to 1.1 for all $T > T_\Theta$. At $T \leq T_\Theta$, ν should drop to the value it would assume for a more compact phase, and ultimately to a value of $2/3$. The above considerations apply, of course, only in the limit of an infinite chain. It was observed by Domb[29] and McCrackin et al.[20] that as the Θ temperature is approached from above, longer and longer chains are needed before the asymptotic estimate for the exponents γ and ν are realized. (The "effective" exponent ν and its dependence on temperature and on chain length can be obtained from the reported values of the ratios $\langle S_n^2 \rangle / \langle r_n^2 \rangle$.) Thus, for short chains, there might not be a unique Θ temperature. The Θ temperature, defined here as the point at which the mean square radius of gyration is a linear function of the degree of polymerization, could depend, in the case of polymers of low molecular weight, on the molecular weight. However, in our experiment, the polymer is of sufficiently high molecular weight, so that the asymptotic behavior is obtained, and a unique Θ temperature, at which chain undergoes a phase transition, can be realized.

Conclusion

The main purpose of this work is to justify the underlying assumptions made in derivation of the polymer chain scattering function $P(\mu)$. In particular, we pay attention to the asymptotic equations for $P(\mu)$, since it is only for large values of the experimentally determined scattering variable x that the results are meaningful and conclusions about the long-range chain interactions (e.g., volume exclusions) can be made. In the derivation of the equation for $P(\mu)$, certain assumptions, out of necessity, must be made. The validity of these assumptions is tested by Monte-Carlo computations. First, we tested the assumption that the second moments $\langle r_{ij}^2 \rangle_N$ and the derived averages (e.g., mean square radius of gyration) depend on $|i - j|$ only. This assumption is found to be reasonably accurate, particularly when the averages over i and j are taken. Next, the assumption that the distribution function for the vector $\mathbf{r}_{ij}$ has a simple limiting form, given by eq 12, is tested. This test is made by computing various higher order reduced moments via Monte-Carlo method and comparing these results with the results one would expect to obtain from the above-made assumption.

There is another important theoretical conclusion, which is corroborated by the experimental evidence.

In good solvents, owing to the segment–solvent interactions, the mean square end-to-end distance and the mean square radius of gyration are known to vary as N^γ, $\gamma > 1$. However, it is not the parameter γ that is determined from the scattering function $P(\mu)$ and its dependence on the scattering angle. It is another effective parameter, ν, which governs the dependence of $\langle r_{ij}^2 \rangle / \langle r_N^2 \rangle$ on $|i - j|$, which is related to the scattering function. The value of this parameter, which determines the limiting values of reduced second-order moments, such as $\langle S_N^2 \rangle / \langle r_N^2 \rangle$, as N tends to infinity, is subject to experimental determination. We found that $\nu = 1.1$ represents the best value, which is also consistent with Monte-Carlo calculations of reduced moments for self-avoiding chains and with the approximate form for the correlation function between any two segments in a chain. Recently conducted experiments on light scattering by solutions of very high molecular weight polymers in good solvents seem to verify this conclusion.

This agreement between the theoretical analysis of the asymptotic scattering function and the experimental findings is restated as follows.

In the limit of large molecular weight and large scattering angle, the exponent which governs the dependence of the scattering function on x, which is the product of the z average squared radius of gyration and of the square of the magnitude of the scattering vector, depends only on the correlation between any two segments in a chain.

In this work, Monte-Carlo computations were used not only for the purpose of computing long-range order interactions in polymer chains as is frequently done in the literature, but, more important, in order to test the validity of various approximations which, out of sheer necessity, are introduced into the theoretical models of polymer chains.

Appendix

Asymptotic Scattering Function for Monodisperse Systems. Equations 20, 22, and 23 lead to the following equation for the scattering function $P(\mu)$, valid in the limit of large N

$$P(\mu) = 4C^3\pi^{-1/2}\int_0^\infty \mathrm{d}r \int_0^1 (1-y)\frac{\sin(\mu r)}{y^{3\nu/2}\mu r}\frac{r^2}{\langle r_N{}^2\rangle^{3/2}} \times F(Cry^{-\nu/2}\langle r_N{}^2\rangle^{-1/2})\mathrm{d}y \quad \text{(A-1)}$$

with $y = |i - j|/N$. In writing (A1), the additional assumption is made that

$$\langle r_{ij}{}^2\rangle_N = \left(\frac{|i-j|}{N}\right)^\nu \langle r_N{}^2\rangle \quad \text{(A-2)}$$

The constant C is determined from the calculated second moment. For gaussian distribution, $C = (3/2)^{1/2}$. For an exponential distribution with exponent δ, that is, for $F(z) = \exp(-z^\delta)$, $C = [\Gamma(5/\delta)/\Gamma(3/\delta)]^{1/2}$. The shape function $F(z)$ is as yet undetermined, except that it is a function of the reduced variable $r/\langle r_{ij}{}^2\rangle_N{}^{1/2}$ and that it decreases exponentially when r tends to infinity, to ensure the convergence of the integrals in (A1).

Introduce a new variable into (A1),

$$z = Cry^{-\nu/2}\langle r_N{}^2\rangle^{-1/2}$$

to obtain

$$P(\mu) = 4C\pi^{-1/2}\langle r_N{}^2\rangle^{-1/2}\int_0^\infty \mathrm{d}z \int_0^1 \frac{(1-y)zF(z)}{\mu y^{\nu/2}} \times \sin(C^{-1}y^{\nu/2}\langle r_N{}^2\rangle^{1/2}\mu z)\,\mathrm{d}y \quad \text{(A-3)}$$

Let $P(\mu) = P_{\mathrm{I}} - P_{\mathrm{II}}$, where P_{I} is the first term in (A3), P_{II} the second one. Consider the limiting case of $\mu\,\langle r_N{}^2\rangle^{1/2} \to \infty$. The limit $P_{\mathrm{I}}{}^* = \lim_{x\to\infty} P_{\mathrm{I}}$ can be evaluated for $F(z)$ given by

$$F(z) = z^l \exp(-z^\delta) \quad \text{(A-4)}$$

as follows. Integrate eq A-3 over z. The integration over z can be performed in closed form, and the integral is replaced by the incomplete γ function. In ref 17 it was shown that in the limit of $\mu\langle r_N{}^2\rangle^{1/2} \to \infty$, this incomplete γ function can be replaced by the complete γ function, which is independent of the variable y. In this case, the integration over y can be readily performed. Since

$$\int_0^\infty x^{-t}\sin x\mathrm{d}x = \Gamma(1-t)\sin\left[\frac{\pi}{2}(1-t)\right] \quad \text{(A-5)}$$

$$\text{for } 0 < t < 1$$

we obtain from (A-3) and (A-5)

$$P_{\mathrm{I}}{}^* = \frac{8\Gamma\left(\frac{2}{\nu}-1\right)\sin\left[\frac{\pi}{2}\left(\frac{2}{\nu}-1\right)\right]}{\nu\pi^{1/2}[C^{-1}\mu\langle r_N{}^2\rangle^{1/2}]^{2/\nu}}G \quad \text{(A-6)}$$

G is the integral

$$G = \int_0^\infty F(z)z^{2-2/\nu}\,\mathrm{d}z = \Gamma\left[\frac{(l+1)(\nu-2)}{\delta\nu}\right] \quad \text{(A-7)}$$

for $F(z)$ given by eq A-4.

According to eq 43, $\langle r_N{}^2\rangle = (1+\nu)(2+\nu)\langle S_N{}^2\rangle$. Since $x = \mu^2\langle S_N{}^2\rangle$, one obtains

$$\lim_{x\to\infty} P(\mu) = Ax^{-1/\nu} \quad \text{(A-8)}$$

For $l = 0$, the coefficient A can be shown to be

$$A = \frac{\pi^{1/2}\Gamma(1/\nu)}{\Gamma(3/\delta)}\left[\frac{4\Gamma(5/\delta)}{(1+\nu)(2+\nu)\Gamma(3/\delta)}\right]^{1/\nu} \times \frac{\Gamma((3\nu-2)/\delta\nu)}{\Gamma((3\nu-2)/2\nu)} \quad \text{(A-9)}$$

For gaussian coils ($\nu = 1$, $\delta = 2$), $A = 2$.

We just showed that for the distribution $F(z)$ given by eq A-9, eq A-8 represents the solution of eq A-1 in the limit of $x \to \infty$. However, the same conclusion can be obtained for other forms of $F(z)$ (e.g., $F(z)$ given in the form of an exponential integral).

Evaluation of B in eq 24 is more involved. Direct substitution results in the following equation for P_{II}.

$$P_{\mathrm{II}} = 8\pi^{-1/2}\nu^{-1}(C^{-1}\mu\langle r_N{}^2\rangle^{1/2})^{-4/\nu}\int_0^\infty \mathrm{d}z \times \int_0^{C^{-1}\mu\langle r_N{}^2\rangle^{1/2}} z^{2-4/\nu}V^{4/\nu-2}F(z)\sin V\mathrm{d}V \quad \text{(A-10)}$$

where $F(z)$ is given by eq A-4. In evaluating $P_{\mathrm{II}}{}^*$, the asymptotic form of eq A-10, it is necessary to follow the procedure adopted in ref 17, namely, start with eq A-1 and integrate over y by parts. The value of P_{II} in the limit of $(\mu/C)\langle r_N{}^2\rangle^{1/2} \to \infty$ is

$$P_{\mathrm{II}}{}^* = \lim_{x\to\infty} P_{\mathrm{II}} = Bx^{-2/\nu} \quad \text{(A-11)}$$

For $F(z) = \exp(-z^\delta)$, the following equation for B is derived in ref 18:

$$B = \frac{\pi^{1/2}}{\nu}\left[\frac{4\Gamma(5/\delta)}{(1+\nu)(2+\nu)\Gamma(3/\delta)}\right]^{2/\nu} \times \frac{\Gamma(2/\nu)\Gamma((3\nu-4)/\delta\nu)}{\Gamma(3/\delta)\Gamma((3\nu-4)/2\nu)} \quad \text{(A-12)}$$

The expansion of $P(\mu)$, valid for large values of x, is restricted to the first two terms. The exponents of x in this expansion were shown to depend on ν only. One still has to consider the remainder to the asymptotic equation for $P(\mu)$. It is clear that for a gaussian distribution, the remainder is of the order of e^{-x}. For the distribution employed in ref 17 that is, for $F(z) = \exp(-z)^\delta$, the remainder was shown to be negligible, provided that $\delta > 2$ and $\nu > 1$.

Difficulty arises when one employs the distribution function proposed by Domb, Gillis, and Wilmers[6b] for $F(z)$, i.e.

$$F(z) = z^{0.5}\exp(-z^\delta)$$

Using the method in ref 17, Utiyama, Tsunashima and Kurata[30] found an additional term in $P(\mu) = P_{\mathrm{I}}{}^* - P_{\mathrm{II}}{}^*$ which is proportional to $\sin(\pi l/2)x^{-(3+l)/2}$. Thus, the exponent of x in this additional term is seen to depend on the shape of the distribution function. Our computations did show that this term is nonnegligible, unless x is very large and both ν

and l exceed their random coil values (that is, above the polymer chain "Θ" point).

Since this work deals only with the first term for $P(\mu)$, in the limit of $x \rightarrow \infty$, the exact expressions for A and B and for the coefficient of $x^{-(3+l)/2}$ are of secondary importance. It suffices to state that these coefficients can be readily expressed in closed form, for a wide variety of the shape functions $F(z)$. However, the fact that the two-term (for $l = 0$) or the three-term (for $l > 0$) asymptotic equation for the scattering function depends both on the shape of the distribution function and the polydispersity of the polymer makes it more imperative to restrict analytical considerations to polymers of very high molecular weight.

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Some Aspects of Water Clusters in Polymers

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ABSTRACT: Cluster theory has been applied to gain new insights into the relationships of water molecules adsorbed in polymers to each other and to the polymer. In many polymers at low relative humidities, it appears that two or more water molecules must interact to make a substantial contribution to the partial pressure. In polymethyl methacrylate, nylon, and cellulose beyond a certain point, newly adsorbed water forms bridges between previously uncorrelated water molecules to reduce the number and increase the size of the clusters. In serum albumin at higher relative humidities, water is added to previously absorbed water molecules to increase the average cluster size from one to two without changing the number of clusters.

Sorption isotherms for water in polymers frequently have a characteristic sigmoidal shape. At low relative humidities, the curve is concave toward the humidity axis showing that polymer–water contacts are favored. At high humidities, the curve is convex toward the humidity axis. In this range, there is a tendency for water molecules to be in contact with each other. Among the theoretical isotherms which have been presented to describe these phenomena are those of Brunauer, Emmett, and Teller[1] and White and Eyring.[2]

An approach to determining the degree of clustering or nonrandom mixing in a two-component system was developed by Zimm[3] following the work of Kirkwood and Buff[4] and applied to mixtures of polymers and solvents by Zimm and Lundberg.[5] This treatment is especially attractive, because it does not depend on any preconceived model. Its application to the sorption of water in a number of polymers has been discussed in an earlier note.[6]

The mean number of water molecules in the neighborhood of a given water molecule in excess of the mean concentration of water is given by

$$c_1G_{11} = (1-\phi_1)\left(\frac{\partial \ln \phi_1}{\partial \ln a_1}\right)_{p,T} - 1 \qquad (1)$$

where G_{11} is the cluster integral, and c_1, ϕ_1, and a_1 are the molar concentration, volume fraction, and activity of water. From this expression, it follows that the average number of water molecules in a cluster may be taken to be $c_1G_{11} + 1$, at least at high relative humidities. At low humidities this quantity may be less than unity, because the tendency to form polymer–water contacts may cause the water molecules to be more isolated from each other than they would be in a random mixture.

The effect of the surface/volume ratio is very small. Assuming that at most three molecular layers, say 10 Å, of water are absorbed on the surface of a fiber 0.2 mils (5 μ) in diameter or a film 1-10 mils thick, the maximum volume fraction of surface water would be 10^{-5}–10^{-3}.

Crystallinity would have a serious effect on the calculation only if the crystalline or water inaccessible fraction changed reversibly with relative humidity, and this is not known to happen. The effect of irreversible changes can be minimized by using the desorption isotherm. The choice of the entire polymer or the amorphous fraction has surprisingly little effect on the value of the clustering function. The sorption isotherm and the clustering function which is derived from it do not depend on anisotropy or orientation, per se.