The calculations were carried out for $\omega = 0$, and $\varphi = 0°, \pm120°$, *i.e.*, for $\Delta\varphi = 0°$ in eq 13. The ratio for the tetrahedral chain ($\theta = 70.5°$) increases monotonically with n toward the limiting value of 2.00 for a two-dimensional chain. For small departures from the tetrahedral angle, the ratio passes through a maximum; the propensity for two-dimensional propagation of the chain over sequences of limited length is dominant for small or intermediate values of n, but, as n increases further, the small departures from strict confinement to two dimensions prevail, and the ratio diminishes eventually to a limiting value of five-thirds. For θ values less than about 60°, the maximum disappears.

The dashed curve in Figure 10 illustrates the effect of displacements of the rotational states by amounts $\Delta\varphi = 5°$, these displacements from the symmetrical positions adopted above being introduced according to eq 13. Even this small alteration of the rotational states suffices to eliminate the maximum.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force of Scientific Research Contract No. F 44620-69-C-0058.

Small-Angle X-Ray Scattering by Polymer Chains in the Submolecular Range

Y. Fujiwara and P. J. Flory

Department of Chemistry, Stanford University, Stanford, California 94305.

Received December 26, 1969

ABSTRACT: Functions describing the angular dependence of the intensity of radiation scattered by chain molecules are calculated on the basis of realistic rotational-isomeric-state models for polymethylene, and for both isotactic and syndiotactic vinyl chains. Numerical calculations are carried out for the submolecular range in which $\mu^2 = (4\pi/\lambda)^2 \sin^2(\vartheta/2)$ is much greater than the reciprocal square radius of the chain. The potentialities of small-angle X-ray scattering as a means of investigating the configurational characteristics of chain molecules are examined. The theoretical treatment is susceptible to major simplification owing to the virtual independence of the mean-square distance $\langle r_{ij}^2\rangle$ between a pair of chain atoms separated by a given number m of bonds ($m = i - j$) on the position of the sequence i,j in the chain. However, values of higher even moments $\langle r_{ij}^4\rangle$, etc., are required for an accurate representation of the scattering function for $\mu > 0.05$–0.10, *i.e.*, the range in which the scattering function is most sensitive to details of the chain configuration.

The theoretical treatment of Rayleigh scattering by chain molecules with realistic account of their structures has been reexamined recently[1,2] with the aid of new methods for treating the configurational characteristics of chain molecules. We have discussed in some detail the scattering function that is appropriate under conditions such that correlation between all pairs of groups, even including those which are most remote in sequence in the chain, are appreciably significant. In particular, Jernigan and one of us[1,2] have shown how the Debye equation for the scattering function, $P(\mu)$, or $P(\vartheta)$, for a freely jointed chain can be modified to render it applicable to real polymer chains. Further refinements can be achieved through computation of sums over the higher moments $\langle r_{ij}^4\rangle$ of the distance between chain atoms i and j.[1,2] It was shown that corrections thus introduced often may be quite negligible.

Here we focus attention on radiation scattering under conditions, usually attainable only with X-radiation, such that the pairs of groups i,j whose correlations contribute most significantly to the scattering function are separated by numbers of bonds $m = i - j$ which are much less than the total length of the chain. This subject has been discussed extensively by Kratky[3,4] and by Kirste[5] and their coworkers. It is the purpose of this paper to bring into account the molecular structure of the chain in question, and its spatial configuration, in a realistic fashion without reliance on artificial models or assumptions lacking sound physical justification. The calculations here presented are intended to be indicative of the potentialities, and limitations as well, of small-angle X-ray scattering as a method for investigating the spatial configurations of chain molecules in general.

Theory

The dependence of the intensity of radiation scattered by a system of unoriented molecules on the angle ϑ from the incident beam and on the wavelength λ (in the scattering medium) is given by the well-known Debye equation[6]

$$P(\mu) = \sum_{i,j} f_i f_j (\mu r_{ij})^{-1} \sin(\mu r_{ij}) \Big/ \sum_{i,j} f_i f_j \qquad (1)$$

where f_i and f_j are the scattering factors for atoms or groups i and j, respectively; r_{ij} is the distance between groups i and j; and

---

[1] P. J. Flory and R. L. Jernigan, *J. Amer. Chem. Soc.*, **90**, 3128 (1968).

[2] P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969; see especially Chapter IX.

[3] O. Kratky, *Pure Appl. Chem.*, **12**, 483 (1965).

[4] O. Kratky, *Kolloid-Z.*, **182**, 7 (1962).

[5] R. G. Kirste, *Makromol. Chem.*, **101**, 91 (1967); V. W. Wunderlich and R. G. Kirste, *Z. Elektrochem.*, **68**, 646 (1964).

[6] P. Debye, *Ann. Physik.*, **46**, 809 (1915).

$$\mu = (4\pi/\lambda) \sin (\vartheta/2) \qquad (2)$$

The scattering function $P(\mu)$ expresses the ratio of the reduced intensity $R(\vartheta,\lambda)$ observed at angle ϑ (and corrected for polarization) to the scattered intensity for $\vartheta = 0$. That is, by definition

$$P(\mu) = R(\vartheta,\lambda)/R(0,\lambda) \qquad (3)$$

For a chain molecule consisting of a linear sequence of atoms or groups, it is usually permissible to take all f_i to be the same. It is necessary, however, to replace $(\mu r_{ij})^{-1} \sin (\mu r_{ij})$ in eq 1 by its average over all configurations of the chain molecule.[7] With introduction of these modifications appropriate for a chain molecule comprising $n + 1$ groups connected by n skeletal bonds, eq 1 can be written[2]

$$P(\mu) = (n + 1)^{-2}\sum_{i,j} G_{ij}(\boldsymbol{\mu}) \qquad (4)$$

where

$$G_{ij}(\boldsymbol{\mu}) = \langle(\mu r_{ij})^{-1} \sin (\mu r_{ij})\rangle \qquad (5)$$

The angle brackets denote the statistical mechanical average taken over all configurations of the chain. That is

$$G_{ij}(\boldsymbol{\mu}) = \int (\mu r_{ij})^{-1} \sin (\mu r_{ij}) W(\mathbf{r}_{ij})\, d\mathbf{r}_{ij} \qquad (6)$$

$W(\mathbf{r}_{ij})$ being the distribution function for the vector $\mathbf{r}_{ij}$ connecting skeletal atoms i and j. The function $G(\mathbf{r}_{ij})$ is just the three-dimensional Fourier transform of $W(\mathbf{r}_{ij})$. As such, it may be developed as a series in the even moments of $\mathbf{r}_{ij}$. Or, following Nagai,[8] it may be expressed as follows as the product of the Gaussian approximation to the Fourier transform and a series in the higher moments of $\mathbf{r}_{ij}$[8,9]

$$G_{ij}(\boldsymbol{\mu}) = \exp(-\mu^2\langle r_{ij}^2\rangle/6)\,[1 + g_2(\mu^2\langle r_{ij}^2\rangle/3) + g_4(\mu^2\langle r_{ij}^2\rangle/3)^2 + \ldots] \qquad (7)$$

where

$$\left.\begin{aligned} g_2 &= 0 \\ g_4 &= -\frac{1}{2^3}\left(1 - \frac{3\langle r_{ij}^4\rangle}{5\langle r_{ij}^2\rangle^2}\right) \\ g_6 &= -\frac{1}{2^4}\left[\left(1 - \frac{3\langle r_{ij}^4\rangle}{5\langle r_{ij}^2\rangle^2}\right) - \frac{1}{3}\left(1 - \frac{9\langle r_{ij}^6\rangle}{35\langle r_{ij}^2\rangle^3}\right)\right] \\ g_8 &= -\frac{1}{2^6}\left[\left(1 - \frac{3\langle r_{ij}^4\rangle}{5\langle r_{ij}^2\rangle^2}\right) - \frac{2}{3}\left(1 - \frac{9\langle r_{ij}^6\rangle}{35\langle r_{ij}^2\rangle^3}\right) + \frac{1}{6}\left(1 - \frac{3\langle r_{ij}^8\rangle}{35\langle r_{ij}^2\rangle^4}\right)\right] \end{aligned}\right\} \qquad (8)$$

etc.[9]

Jernigan and one of us[10] have shown by numerical calculations that the second moments $\langle r_{ij}^2\rangle_0$ for polymethylene chains when unperturbed by external forces or by excluded volume effects (this being denoted by the subscript zero) are essentially determined by the magnitude of $i - j$, *i.e.*, by $m = |i - j|$; the location of the sequence $i - j$ within the chain has only a trivial effect on the value of $\langle r_{ij}^2\rangle_0$. Even in the extreme case where $i = 0$ and $j = n$, $\langle r_{0n}^2\rangle_0$ (*i.e.*, $\langle r_n^2\rangle_0$ with $n = m$) differs inconsequentially from $\langle r_{ij}^2\rangle_0$ for a sequence $|i - j|$ of the same length (n) within a chain of infinite length.[10] The greatest difference occurs for $n = 3$, and here it is only about 6%.

TABLE I

COMPARISON OF CHARACTERISTIC RATIOS C_m FOR FINITE ISOTACTIC CHAINS WITH RATIOS C_{ij} FOR CORRESPONDING SEQUENCES IN INFINITE CHAINS[a]

	$\omega = 0.001$		$\omega = 0.010$		$\omega = 0.100$	
m	C_m	C_{ij}^∞	C_m	C_{ij}^∞	C_m	C_{ij}^∞
3	1.650	1.740	1.650	1.746	1.650	1.750
4	2.104	2.104	2.098	2.102	2.046	2.081
5	2.398	2.460	2.393	2.446	2.341	2.390
10	3.951	4.616	3.880	4.260	3.448	3.533
20	7.482	8.595	6.810	7.123	4.697	4.740
∞	55.69	55.69	18.09	18.09	6.496	6.496

[a] Calculations carried out for $\eta = 1.0$, $\tau = 0.5$, and the several values of ω indicated.

Similar calculations for isotactic vinyl chains are presented in Table I. Here we compare the characteristic ratio $C_m = \langle r_m^2\rangle_0/ml^2$ for a chain $CH_3(CHRCH_2)_{m/2}H$ of m bonds with $C_{ij}^\infty = (\langle r_{ij}^2\rangle_0/|i - j|l^2)_\infty$ for a corresponding sequence of $|i - j| = m$ bonds within an infinite chain. The calculations were carried out for the several values of ω and m indicated. (For $m = 1$ and 2, the two quantities are necessarily equal.) Differences are less than 10% for $\omega \geq 0.010$. For syndiotactic chains the differences would be even smaller.

In light of these results and those of Jernigan[10] cited above, we may, with negligible error for unperturbed chains, identify $\langle r_{ij}^2\rangle_0$ with $\langle r_m^2\rangle_0$, where the former quantity represents any sequence consisting of $|i - j| = m$ consecutive bonds irrespective of the location of the sequence within the chain or of the length of the chain as a whole. This identification permits major simplification of the treatment of radiation scattering by polymeric chain molecules.[1,2] It is employed throughout the following development. Inasmuch as this identification is strictly valid only for unperturbed chains, the development is addressed primarily to chains in environments (*e.g.*, in Θ solvents) where this condition is met.

We shall assume further that the higher moments $\langle r_{ij}^4\rangle_0$, $\langle r_{ij}^6\rangle_0$, etc., may likewise be replaced by $\langle r_m^4\rangle_0$, etc. Direct numerical calculations in support of these substitutions have not been carried out, but their legitimacy can scarcely be questioned in light of the close correspondences for the second moments. Moreover, the higher moments enter only as correction terms (*cf.* the following). They do not, therefore, need to be evaluated with the same accuracy as required for the second moment.

Simplification of eq 4 through introduction of this well-justified approximation yields[1,2]

$$P(\mu) = (n + 1)^{-1} + 2(n + 1)^{-2} \sum_{m=1}^{n}(n + 1 - m)G_m(\boldsymbol{\mu}) \qquad (9)$$

---

[7] P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).

[8] K. Nagai, *J. Chem. Phys.*, **38**, 924 (1963).

[9] See ref 2, pp 309–311, 344–345. The general expression for higher coefficients g_{2p} is given in this reference.

[10] R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **50**, 4165 (1969). See also ref 2, pp 147–148.

where $G_m(\boldsymbol{\mu})$ is the Fourier transform of the distribution function $W(\mathbf{r}_m)$ for the vector spanning a sequence of m bonds. It is given by eq 7 and 8 with $\langle r_{ij}^{2p}\rangle$ therein replaced by $\langle r_m^{2p}\rangle_0$ where $m = |i - j|$.

Instead of $P(\mu)$, we shall prefer the function $F_n(\mu)$ defined by

$$F_n(\mu) = (n + 1)\mu^2 P(\mu) \tag{10}$$

According to eq 9 and 7

$$F_n(\mu) = \mu^2 + 2\mu^2(n + 1)^{-1}\sum_{m=1}^{n}(n + 1 - m)G_m(\boldsymbol{\mu}) =$$
$$\mu^2 + 2\mu^2(n + 1)^{-1}\sum_{m=1}^{n}(n + 1 - m)\exp(-\mu^2\langle r_m^2\rangle_0/6) \times$$
$$[1 + g_4(\mu^2\langle r_m^2\rangle_0/3)^2 + g_6(\mu^2\langle r_m^2\rangle_0/3)^3 + \ldots] \tag{11}$$

where g_4, g_6, etc., are defined according to eq 8 with the moments $\langle r_{ij}^{2p}\rangle$ replaced by $\langle r_m^{2p}\rangle_0$, as specified above.

Equations 9 and 11 for the alternative scattering functions $P(\mu)$ and $F_n(\mu)$ rest on the following assumptions and approximations: (i) absence of multiple scattering, (ii) intermolecular independence (*i.e.*, absence of correlations between different molecules in the solution), (iii) elastic scattering, (iv) treatment of each of the $n + 1$ groups as a point scatterer, (v) equivalence of all $\langle r_{ij}^2\rangle_0$ with $|i - j| = m$ to $\langle r_m^2\rangle_0$ as noted above, and (vi) absence of long-range perturbations of the molecular configuration. Fulfillment of conditions i and ii is assured at sufficient dilutions. Effects of condition iii are generally unimportant in X-ray scattering; they may be circumvented in light-scattering experiments by measuring the combined intensities of all scattered radiation including incoherent radiation of slightly displaced frequency.[11] The point scatterer approximation (iv) must be kept foremost in mind for large values of μ such as may be attained with X-rays at angles ϑ of several degrees, giving Bragg distances on the order of 20 Å or less. The limitations set by condition iv are minimal for polymethylene chains wherein the preponderance of the electrons are closely associated with identical scattering centers, namely, the skeletal carbon atoms. They may be more restrictive for chains bearing large substituents, *e.g.*, for vinyl chains. Even here, present methods could readily be elaborated to take account of substituents as separate scattering centers.[12] According to the numerical calculations cited earlier, in the range of μ for which condition iv is justified, fulfillment of condition v is virtually guaranteed for sequences of the length m which, at such values of μ, affect the scattering function significantly. Condition vi is obviously restrictive. However, for $\mu^2 \gg 1/\langle s^2\rangle$, *i.e.*, for combinations of scattering angle and wavelength such that the square of the Bragg distance is much less than the mean square radius of gyration $\langle s^2\rangle$ of the molecule, perturbations of the chain configuration by long-range interactions should be of minor importance, and it may actually be permissible to ignore them. Thus, for sufficiently large values of μ, the present theory may be applied to molecules which are subject to perturbations of long range (*i.e.*, subject to the effects of excluded volume.)

As later calculations show, higher terms of the series in eq 11 may sometimes be disregarded. When this is the case, eq 11 can be simplified to

$$F_n(\mu) = \mu^2 + 2\mu^2(n + 1)^{-1}\sum_{m=1}^{n}(n + 1 - m) \times$$
$$\exp(-\mu^2\langle r_m^2\rangle_0/6) \tag{12}$$

which may be evaluated numerically from computed values of $\langle r_m^2\rangle_0$ for chains of total length $n = m$.

The mean-square end-to-end distance $\langle r_m^2\rangle_0$ often is assumed to be linear in the chain length. As previous calculations for real chains show,[2,13-15] this approximation is acceptable only for long chains. It is instructive, nevertheless, to examine the consequences of its incorporation into eq 12. To this end, we let

$$\langle r_m^2\rangle_0/6 \approx Am - B \tag{13*}$$

where A and B are treated as constants. Obviously, A is directly related to the limiting value of the characteristic ratio $C_\infty = (\langle r^2\rangle_0/nl^2)_{n\rightarrow\infty}$, l being the bond length; *i.e.*

$$A = l^2C_\infty/6 \tag{14}$$

Substitution of eq 13* into 12 and evaluation of the sum gives

$$F_n^*(\mu) = \mu^2 + \frac{2\mu^2\exp[(B - A)\mu^2]}{1 - \exp(-A\mu^2)} \times$$
$$\left\{1 - \frac{1 - \exp[-(n + 1)A\mu^2]}{(n + 1)[1 - \exp(-A\mu^2)]}\right\} \tag{15}$$

The asterisk signifies incorporation of the approximation represented by eq 13*, and eq 15 is subject to the same approximation; its derivation from eq 12 and 13* is exact. For chains of great length, *i.e.*, for $n \rightarrow \infty$, we have from eq 15

$$F_\infty^*(\mu) = \mu^2 + 2\mu^2\exp[(B - \mathrm{A})\mu^2]/[1 - \exp(-A\mu^2)] \tag{16}$$

and in the limit of vanishing μ

$$F_\infty(0) = 2/A = 12/l^2C_\infty \tag{17}$$

The asterisk is here omitted inasmuch as the approximation entailed in eq 13* vanishes in the limit $\mu = 0$.

For a freely jointed chain $B = 0$ in eq 13*, and we have the results

$$F_n^\dagger(\mu) = \mu^2 + \frac{2\mu^2\exp(-A\mu^2)}{1 - \exp(-A\mu^2)} \times$$
$$\left\{1 - \frac{1 - \exp[-(n + 1)A\mu^2]}{(n + 1)[1 - \exp(-A\mu^2)]}\right\} \tag{18}$$

---

(11) R. Pecora, *J. Chem. Phys.*, **49**, 1032, 1036 (1968).

(12) More complicated chains comprising several kinds of atoms and groups are readily susceptible to treatment by present methods. The several kinds of scattering centers, which may occur in side chains as well as in the chain backbone, may be distinguished according to their scattering powers and their structural connections. It is required merely to execute a separate summation for each pairwise combination from the several types of scattering centers. The computational labor increases of course according to the number of such pairwise combinations that must be distinguished.

(13) P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

(14) R. L. Jernigan and P. J. Flory, *ibid.*, **50**, 4178 (1969).

(15) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 280 (1970).

and

$$F_\infty^\dagger(\mu) = \mu^2 + 2\mu^2 \exp(-A\mu^2)/[1 - \exp(-A\mu^2)] \quad (19)$$

where the superscript dagger denotes the freely jointed chain.[16]

To facilitate numerical computations it is convenient to define the quantity

$$\Delta_m = G_m(\mathbf{\mu}) - \exp(-Am\mu^2) \quad (20)$$

or, if higher terms in the series expansion of $G_m(\mathbf{\mu})$ are neglected (see eq 7)

$$\Delta_m = \exp(-\mu^2\langle r_m^2\rangle_0/6) - \exp(-Am\mu^2) \quad (21)$$

where A is related to the limiting characteristic ratio according to eq 14. Then

$$F_n(\mu) = F_n^\dagger(\mu) + [2\mu^2/(n + 1)]\sum_{m=1}^{n}(n + 1 - m)\Delta_m \quad (22)$$

and for a chain of sufficient length

$$F_\infty(\mu) = F_\infty^\dagger(\mu) + 2\mu^2 \sum_1^\infty \Delta_m \quad (23)$$

The quantities $F_n^\dagger(\mu)$ and $F_\infty^\dagger(\mu)$ are readily calculable from eq 18 and 19, respectively; the sums in eq 22 and 23 may be evaluated numerically if the characteristic ratio $C_m = \langle r_m^2\rangle_0/nl^2$ is known throughout the range of m, including its limiting value C_∞ required for evaluation of A.

Numerical Calculations

Calculations of $F_\infty(\mu)$ for polymethylene chains (PM) carried out using the same parameters as in the preceding paper[15] and elsewhere[2,10,14,17] ($\theta = 68°$, $\sigma = 0.54$, and $\omega = 0.088$) are presented in Figure 1 for the range $\mu = 0–0.5$. (The upper limit, $\mu = 0.5$, corresponds to a Bragg length of 12.6 Å, and to a Bragg angle $\vartheta/2 = 3.5°$ for X-radiation of wavelength $\lambda = 1.54$ Å.) The second curve from the bottom of the graph was calculated according to eq 11 with the series truncated beyond the term in $(\mu^2\langle r_m^2\rangle_0/3)^2$.[18] The coefficient g_4 of this term depends on the fourth moments $\langle r_m^4\rangle_0$. Values of these moments were taken from the preceding paper.[15] Comparison with the curve calculated according to eq 12 is indicative of the consequences of ignoring all terms beyond unity in the series in eq 11. The difference between the two curves at $\mu = 0.5$ is about 20%. Estimates of g_6, g_8, etc., using the higher moment ratios $\langle r_m^6\rangle_0/\langle r_m^2\rangle_0^3$, etc., computed by Nagai[19] for PM chains, indicate that inclusion of higher terms of the series in eq 11 would further lower F_∞ by about 10% at $\mu = 0.5$. These corrections become smaller as μ diminishes, as indicated by comparison of the respective curves in Figure 1 calculated according to eq 12 and eq 11 (with truncation beyond g_4).

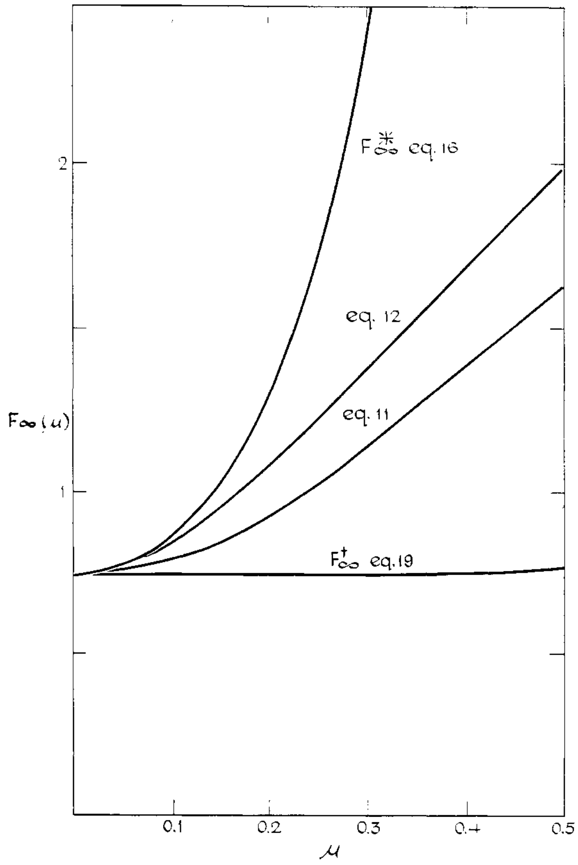

Figure 1. Comparison of the scattering functions $F_\infty(\mu)$ for unperturbed PM chains of infinite length over the range $\mu = 0–0.5$. The four curves were calculated according to the equations indicated. Equation 11 was truncated beyond the term with coefficient g_4 involving the fourth moment $\langle r_m^4\rangle_0$. Parameters used for the calculations are given in the text.

These calculations demonstrate the importance of refinement of the Fourier transform of $G_m(\mathbf{\mu})$ of the distribution function for the purpose of accurately relating submolecular scattering to the constitution and configuration of chain molecules (PM chains specifically) in the range $\mu > \sim 0.05$, *i.e.*, in the range corresponding to Bragg distances less than about 100–150 Å. This is the conclusion of foremost importance to be drawn from the results in Figure 1. Thus, in contrast to the theory of molecular scattering[1,2] applicable for $\mu^2\langle r^2\rangle_0/6 < \sim 3$, where terms in the higher moments $\langle r^4\rangle_0$, etc., may generally be ignored,[20] their neglect incurs appreciable errors in the treatment employed here, which is intended to deal with submolecular scattering.

Concerning the other two curves shown in Figure 1, it will be apparent that F_∞^* calculated according to eq 16, which rests on the assumption of linearity of $\langle r_m^2\rangle_0$ with m (see eq 13*), is unsatisfactory for $\mu > 0.10$. At $\mu = 0.5$ the value of F_∞^* (not included in

---

[16] For $n \gg 1$ and $\mu^2 \ll 1$, eq 18 reduces to the familiar equation of Debye,[7] $n^{-1}\mu^{-2}F_n(\mu) = P(\mu) = (2/v^2)(v - 1 + e^{-v})$, where $v = nA\mu^2$ in present notation. See ref 2, p 346. Equations 18 and 19 are not, of course, subject to these conditions on n and μ.

[17] A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88,** 631 (1966).

[18] These calculations actually were carried out by first finding $F_\infty^\dagger(\mu)$ and then executing the summation specified in eq 23.

[19] K. Nagai, *J. Chem. Phys.*, **48,** 5646 (1968).

[20] As shown elsewhere,[1,2] the Debye equation (see ref 16) may serve to represent molecular scattering well beyond the limits implied by the assumptions in its original derivation,[7] provided, however, that v therein is redefined[1,2] by $v = \mu^2\langle s^2\rangle$, where $\langle s^2\rangle$ is the *perturbed* radius of gyration for the chain of finite length n.

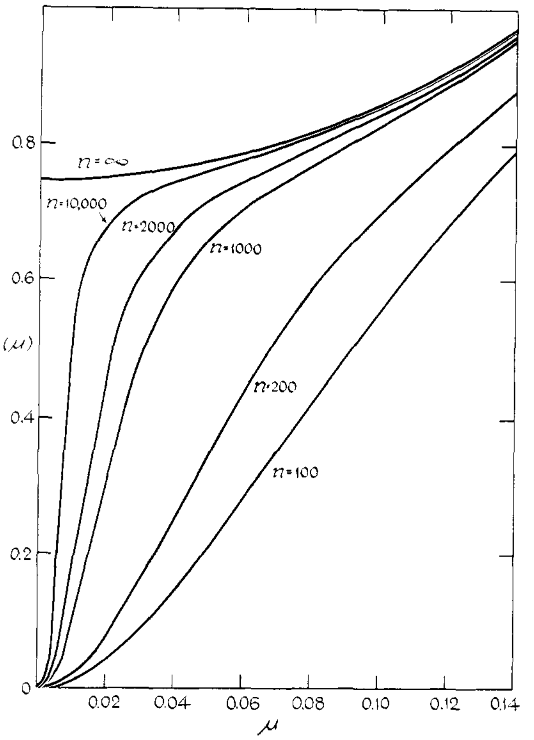

Figure 2. The scattering function $F_n^*(\mu)$ calculated according to eq 15 for finite PM chains of the lengths indicated in the figure.

Figure 1) is in error by a factor of about 10. In fact, $F_\infty^\dagger$ calculated according to eq 19 in the zeroth order approximation of proportionality of $\langle r_m^2 \rangle_0$ to m gives a better account of the scattering function than F_∞^*, calculated on the basis of eq 13*, for all values of $\mu >$ 0.05. Neither of these approximations can be regarded as satisfactory for the range of submolecular scattering, however.

The dependence of $F_n(\mu)$ on μ for polymethylene chains of various lengths n is shown in Figure 2. These curves have been obtained by use of eq 15, its limitations revealed above for $\mu > \sim 0.10$ notwithstanding, in order to avoid the more arduous summations required by eq 11 or 12. The curves in Figure 2 are intended to illustrate the departures from the limiting curve for F_∞^* due to finite length of the chain. The effects are marked in the lower range of μ even for $n = 10^4$. This is just the range where the molecular theory[1,2] rather than the present methods should be employed. In general, when the scattering function $F_n(\mu)$ falls much below $F_\infty(\mu)$, the molecular theory, as represented by the Debye equation[7,16] amended as mentioned earlier,[20] will be preferred.

Scattering functions $F_\infty(\mu)$ for isotactic vinyl chains are shown in Figure 3 for the range μ = 0–0.5. The parameters, $\theta = 68°$, $\eta = 1.0$, and $\tau = 0.5$, chosen in the preceding paper[15] were used throughout, together with the two values of ω indicated in the figure. Curves calculated according to eq 12 are shown dashed; those calculated with inclusion of the term in g_4 in the series in eq 11 are shown as full lines. The curve for PM calculated in the latter manner, and taken from Figure 1, is shown for comparison. The curve for the isotactic polymer with ω = 0.10 approximates that for

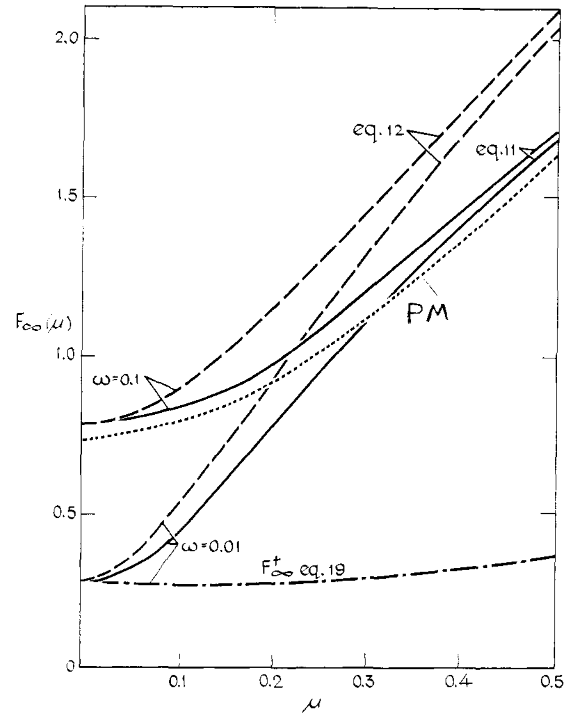

Figure 3. The scattering function $F_\infty(\mu)$ for infinite isotactic chains with ω = 0.01 and 0.10 (and $\theta = 68°$, $\eta = 1.0$, $\tau = 0.5$; see text). Full curves have been calculated according to eq 11 truncated beyond the term with coefficient g_4. Dashed curves have been calculated according to eq 12; the dash–dot curve represents $F_\infty^\dagger(\mu)$ according to eq 19. The dotted curve, taken from Figure 1 for PM calculated using eq 11, is reproduced for comparison.

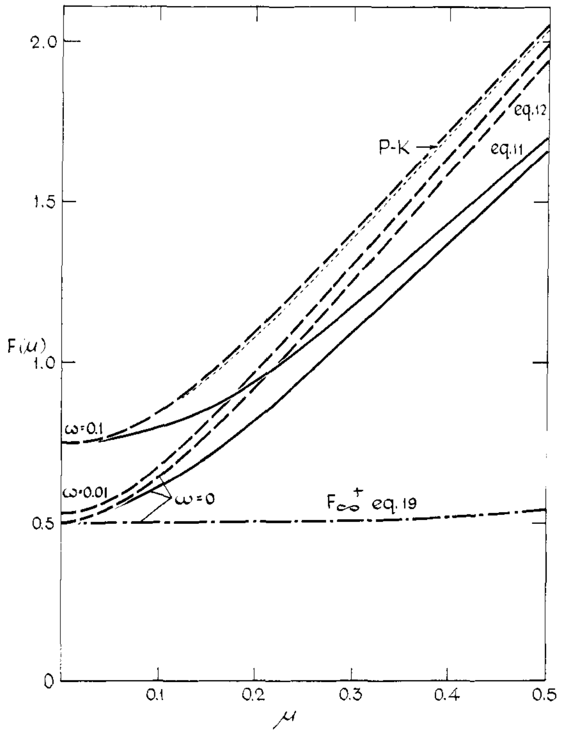

Figure 4. Scattering functions as indicated for syndiotactic chains. Calculations carried out for the Porod-Kratky (P-K) model chain, with parameters L and a chosen arbitrarily, are represented by the dotted curve.

PM, as follows directly from the similarity of moments for the two chains.[15] The corrections contributed by higher terms in the series expansion (see eq 7 and 11) of the Fourier transform $G(\mathbf{\mu})$ are similar to those found for PM (Figure 1) when they are expressed as percentages of $F_\infty(\mu)$.

The lower intercept at $\mu = 0$ for $\omega = 0.01$ compared with that for $\omega = 0.10$ reflects, of course, the greater value of the characteristic ratio in the former case. The steeper rise of this curve with μ is due to (and diagnostic of) the greater "stiffness" of this chain.

Scattering functions similarly calculated for syndiotactic chains are presented in Figure 4. Again, higher terms in the series expansion of the Fourier transform of $W(\mathbf{r}_m)$ are important. The scattering function is less dependent on ω, and this is in keeping with the configurational statistics of syndiotactic chains[2,15,21] whereby the greater diversity of conformations accessible to them renders the tortuosity of the chain, and hence its moments, subject to a lesser dependence on the incidence of nonpreferred conformations permitted to a degree fixed by ω. However, the curves for $\omega = 0$ differ perceptibly from those for $\omega = 0.10$ even at larger values of μ.

Also included in Figure 4 is a curve calculated for the Porod-Kratky chain,[22-24] with parameters arbitrarily chosen to optimize matching of the curve for $\omega = 0.10$, the calculations being carried out in the approximation of eq 12. The fully extended length adopted for that purpose is $L = 0.8290nl$, which, of course, bears no obvious rational relation to the structure of the chain. The choice depends upon prior calculations of moments for the real chain,[15] which are then used to establish the parameters. Once these moments have been calculated, resort to the P-K model is superfluous.

The scattering functions $F_n{}^*(\mu)$ for isotactic chains of finite lengths are compared in Figure 5 with $F_\infty{}^*(\mu)$ over the lower range μ = 0-0.10. The value of ω is 0.01 in each case. Owing to the greater stiffness of these chains, convergence to the curve for $n = \infty$ is more rapid than for PM chains (compare Figure 2). Thus, the submolecular treatment has a greater range of validity for stiff chains. On the other hand, the molecular treatment quite obviously is more restricted in its application to stiff chains, greater chain lengths and smaller values of μ being required for its efficacy.

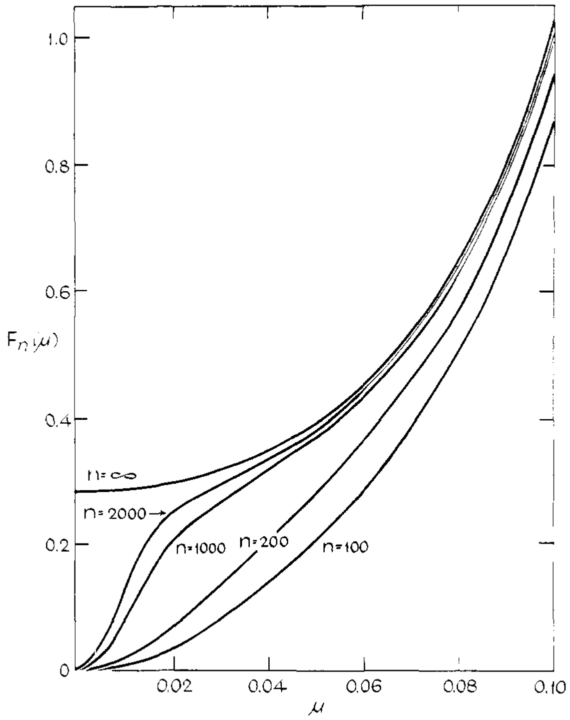

Figure 5. Scattering functions for isotactic chains of finite length. All curves calculated for $\omega = 0.01$.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Contract No. F 44620-69-C-0058.

---

(21) P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966).

(22) G. Porod, *J. Polym. Sci.*, **10**, 157 (1953).

(23) A. Peterlin, *ibid.*, **47**, 403 (1960).

(24) S. Heine, O. Kratky, G. Porod, and P. J. Schmitz, *Makromol. Chem.*, **44/46**, 682 (1961).