Dilute Solution Properties of Randomly Branched Polymer Systems. I. The Particle Scattering Factor

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Revised Manuscript Received August 21, 1973

ABSTRACT: A simpler method than hitherto discussed, based on graph theory, has been proposed to handle the combinatorics of randomly branched polymer systems. This method, using so-called "path-weighting generating functions," has been exploited to derive z-average particle scattering factors for the randomly cross-linked systems of arbitrary primary chain distribution (vulcanisates) which have been described previously. By introducing the stiff chain statistics of Daniels, the submolecular scattering ranges of these systems are studied and it is found that the scattering envelopes are sensitive to the primary chain distributions. The weight-average mean-square radius of gyration is calculated as an example of the application of bivariate path-weighting generating functions.

The traditional combinatorial arguments for physical properties of a branched polymer system are often extensive though elegant[2,3] and little attention has been paid to the effect of molecular weight distribution which is normally extremely broad. Although the molecular weight distribution for various branched polymer systems have been thoroughly discussed,[4] our understanding of the combined effects of branching and polydispersity on various physical properties of these systems is not very advanced. The difficulties in these basic problems are mainly of a combinatorial nature and can be obviated by adapting the stochastic theory of cascade processes, especially developed by Good.[5,6] Gordon[7] gave the first example of this kind of approach in calculating the various molecular weight averages and the gel point of polyfunctional condensates. His method has the advantage over the usual statistical method[8,9] of greatly reducing the use of probability theory by introducing the concept of a statistical forest of molecular trees, defined by the probability generating function (pgf) for the number of offsprings in each generation. The combinatorial labor, once systematized within a graph theoretical framework, is greatly reduced.[10]

When intramolecular effects in polymers are treated in terms of graph theory, the combinatorial problems classify into those concerning one point ("repeat unit") at a time, two at a time, etc., as exemplified by the use of cluster expansions in the theory of intermolecular effects in ordinary liquids. For example, by picking a single repeat unit at random, one may deal with molecular weight distributions. In the theory of radiation scattering from polymer solutions, the most significant term involves pairs of points, although multiple scattering within a polymer molecule necessitates the combinatorics of more than two points. An example of three-point combinatorics is found in theoretical treatments of the second virial coefficient by means of Zimm's double-contact approximation.[11] Here one point lies on each of two adjacent molecules, the third point is shared between them. Although Gordon later extended his theory to problems in two-point combinatorics, such as the radius of gyration,[12,13] his is essentially a single-point method limited to special cases of two-point combinatorics. General two-point problems are treated more directly by utilizing the power of the path-weighting function (pwf), introduced into the pgf.[14-16] The pwf $\phi(n)$ is a function of the length n of a path which is a linear succession of lines within a graph, its length is the number of lines it contains. For example, any three consecutive carbons in an octane define a path of length two. Important physical properties are calculated as the average of some pwf over all distinct paths in a polymer system, and are generated by this new type of generating function, the path-weighting generating function (pwgf).

This paper deals with single-point and particularly with two-point combinatorics of branched polymer systems which are produced by random cross-linking (vulcanization) of primary chain populations with arbitrary chain distributions as in a previous paper,[17] but the theory is presented here in a somewhat different way. The particle scattering factors, especially in the range of submolecular scattering, will be studied in order to find a new way of characterizing polydisperse randomly branched systems.

1. Graph Theory and Chemical Systems

The basic statistics of a branched-chain distribution are formulated within the general framework of the theory of cascade (branching) processes,[18] by representing each molecule as a tree, or connected acyclic graph.[7,12,13] A whole molecular ensemble comprises a molecular forest of these "family trees," and the concept of a clone is introduced in order to formalize the combinatorial analysis. The clone is a new forest of rooted trees produced from the molecular forest above[19] by selecting each repeat unit (node) of each tree in the molecular forest as the root of a tree in the clone where the root forms the zeroth generation. By letting the number of trees in the molecular forest tend to infinity, the clone may be simulated in statis-

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(10) M. Gordon, *Collect. Math. Soc. Janos Bolyai*, **4**, 511 (1969).

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tically equivalent form by generating functions, as in the theory of cascade processes. The algebraic structure of the relevant generating functions can be mapped into the same kinds of trees as branched polymer molecules.[10,14] The number of links in a path is reflected by the number of generations in a molecular tree. Vulcanisates are treated as a general case of y-functional polycondensation by considering the original monomer (primary chain) to consist of a distribution of molecules of varying functionality. An example of this procedure is illustrated by the contraction of Figure 1a to 1b. This essential process, which occurs commonly in graph theory, is called "elementary contraction"[20] and denotes the removal of one line from a graph and subsequent identification of the two points originally joined by that line; that is, the two points are merged into a single point. The tree in Figure 1a is transformed into that in Figure 1b by elementary contraction of all its horizontal lines, *i.e.*, the contraction of each primary chain to a single point. Consequently, the information about primary chain lengths is lost and only cross-links bear the genetic information relating to primary chain connectivity. The classical problems in single-point combinatorics (first treated by Stockmayer[21]) are much simplified by this elementary contraction[9,22] as is demonstrated by the following pgf

$$F_0(\theta) = \sum_{y=1}^{\infty} m_y(1 - \alpha + \alpha\theta)^y \tag{1}$$

$$F_1(\theta) = F_2(\theta) = \cdots = \sum_{y=1}^{\infty} m_y(1 - \alpha + \alpha\theta)^{y-1} \tag{2}$$

Here m_y is the weight fraction of y-mers in the primary distribution and α is the fraction of cross-links per primary chain defined by

$$\alpha = F_0'(1)/DP_n \tag{3}$$

where F_0' is called a cross-linking index[9] and DP_n is the number-average degree of polymerization. The formulation of pgf's for successive generations (eq 2) involves an assumption that no ring formation occurs, *i.e.*, there is not more than one tie (cross-link) between two primary chains in successive generations. Following Good's theory of cascade processes,[5] the weight-fraction generating function, $W(\theta)$, is given by the pgf.

$$W(\theta) = \sum_{y=1}^{\infty} m_y\theta^y(1 - \alpha + \alpha u)^y \tag{4}$$

with the auxiliary variable

$$u = \sum_{y=1}^{\infty} m_y\theta^y(1 - \alpha + \alpha u)^{y-1} \tag{5}$$

and its integral or differential wrt θ evaluated at $\theta = 1$ gives, respectively, the number-average (DP_n) or weight-average (DP_w) degree of polymerization of the whole system. Thus

$$DP_n = \bar{y}_n/(1 - \alpha\bar{y}_n/2) \tag{6}$$

$$DP_w = \bar{y}_w(1 + \alpha)/\{1 - \alpha(\bar{y}_w - 1)\} \tag{7}$$

where $\bar{y}_n$ and $\bar{y}_w$ are the number-average and the weight-average degree of polymerization of the primary chains. The dummy variable θ in the weight fraction gf bears an exponent y because the original monomer has a degree of polymerization y. Gordon omitted this exponent by considering the original monomer as a new unit.[7] Gordon's result for the weight-average degree of polymerization, therefore, needs to be multiplied by $\bar{y}_w$, when one compares his result with that of Stockmayer.[21]

There are two types of ensembles for the cross-linked system treated in this paper according to the different manner of constructing the clone. Ensemble 1 is formed by choosing each primary chain in the system in turn and placing it on the zeroth generation to form the root of a tree, and ensemble 2 by choosing each repeat unit and placing the whole of the primary chain to which it belongs on the zeroth generation. The average size of the chains on the zeroth generation in ensemble 1 is therefore the number-average $\bar{y}_n$ of the primary distribution, while it is the weight-average $\bar{y}_w$ in ensemble 2. Equation 1 shows the pgf for ensemble 2. The pgf for ensemble 1 is obtained on replacing m_y by n_y (the number fraction of y-mers in the primary distribution) in eq 1. The pgf's for subsequent generations are the same for both ensembles (*cf.* eq 2), because one repeat unit is always chosen to be a cross-link with a primary chain in the former generation. Only ensemble 2 will be used for two-point combinatorics, and the interest is focussed on the combinatorics of two repeat units in a molecular tree and not on that of two primary chains. Ensemble 1 was applied by Dobson and Gordon to the calculation of the number and mean length of active network chains.[22] In any ensemble, the randomly formed cross-links alone are assigned to link a pair of primary chains on successive generations and bear the genetic information of the cascade formalism. All repeat units of each primary chain stay on the same generation.

2. pwgf of Ensemble 2

To formulate the pwgf, it is necessary to recover the lost information concerning primary chain length. For this purpose, the requisite enumeration generation function is introduced to replace the pwf. Thus, the pwgf is written with a dummy variable θ as

$$u_0(\theta) = \sum_{y_0=1}^{\infty} m_{y_0}\theta^{B_0(\phi;y_0)}(1 - \alpha + \alpha u_1(\theta))^{y_0} \tag{8}$$

$$u_i(\theta) = \sum_{y_i=1}^{\infty} m_{y_i}\theta^{B_i(\phi;y_0,y_1,\cdots,y_i)}(1 - \alpha + \alpha u_{i+1}(\theta))^{y_i-1} \qquad i > 1 \tag{9}$$

where $B_i(\phi;y_0,y_1,\cdots,y_i)$ is the enumeration generating function in which the coefficient of θ^n is the mean number of paths of the total length n per root in the clone. Such paths start at any repeat unit on g_0 and terminate on some unit of a primary chain g_i, having passed through subchains of a primary chain on g_1, a primary chain on g_2, and so on. The length y_i of a primary chain on generation i features as an independent variable. In eq 8 and 9, the simplest case is assumed for the configurational statistics of subchains

$$\phi(n) = \phi^n \tag{10}$$

The more general case of configurational correlations requires the extended forms

$$u_0(\theta) = \sum_{y_0=1}^{\infty} m_{y_0}\theta^{\sum_n \zeta(\phi^n)[B_0(\phi;y_0)]\phi(n)}(1 - \alpha + \alpha u_1(\theta))^{y_0} \tag{11}$$

$$u_i(\theta) = \sum_{y_i=1}^{\infty} m_{y_i}\theta^{\sum_n \zeta(\phi^n)[B_i(\phi;y_0,y_1,\cdots,y_i)]\phi(n)} \times (1 - \alpha + \alpha u_{i+1}(\theta))^{y_i-1} \qquad i \geq 1 \tag{12}$$

Here $\zeta(\phi^n)[]$ denotes the selection operator of the coefficient of ϕ^n in the enumeration generating function $B_i(\phi;y_0,y_1,\cdots,y_i)$. The latter is itself a product of $i + 1$

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(21) W. H. Stockmayer, *J. Chem. Phys.*, 12, 125 (1944).

(22) G. R. Dobson and M. Gordon, *J. Chem. Phys.*, 43, 705 (1965).

simpler generating functions (the contribution from subchains lying on $i + 1$ successive generations) times ϕ^i (the contribution from i cross-links between the zeroth and the ith generation) by virtue of a convolution theorem (see Appendix). The straightforward application is exemplified by integration or differentiation of the pwgf (eq 8 or 11) with respect to θ at $\theta = 1$.[15,23] When eq 10 applies, the pwgf reduces to the new enumeration generating function for the mean number of distinct paths in a clone, *i.e.*

$$E(\phi) \equiv \left[\frac{\mathrm{d}u_0(\theta)}{\mathrm{d}\theta}\right]_{\theta=1} = \frac{(1 + \alpha\phi)\bar{f}_{\mathrm{w}}(\phi)}{1 - (\bar{f}_{\mathrm{w}}(\phi) - 1)\alpha\phi} \tag{13}$$

where the function $\bar{f}_{\mathrm{w}}(\phi)$ is defined by

$$\bar{f}_{\mathrm{w}}(\phi) = \sum_{y=1}^{\infty} m_y B_0(\phi;y) \tag{14}$$

The meaning of this new generating function is clearly demonstrated by rewriting eq 13 as

$$E(\phi) = \sum_{x,k} w_{xk} x^{-1} (\sum_n 2N_{nxk}\phi^n) \tag{15}$$

where w_{xk} is the weight fraction and N_{nxk} the number of distinct paths of length n in the kth isomer of the x-mer fraction.[15] The function $\bar{f}_{\mathrm{w}}(\phi)$ is expressed in terms of the number fraction generating function of the primary distribution

$$N(\phi) = \Sigma n_y \phi^y \tag{16}$$

thus

$$\bar{f}_{\mathrm{w}}(\phi) = \frac{1 + \phi}{1 - \phi} - \frac{2\phi}{(1 - \phi)^2 \bar{y}_{\mathrm{n}}}[1 - N(\phi)] \tag{17}$$

where n_y is the number fraction of y-mers in the primary distribution. The number fraction generating functions are already known for various distributions. For example, the number fraction for the generalized Schulz distribution is written as[24,25]

$$N(\phi) = [1 - (\bar{y}_{\mathrm{w}} - \bar{y}_{\mathrm{n}}) \ln \phi]^{-\bar{y}_{\mathrm{n}}/(\bar{y}_{\mathrm{w}} - \bar{y}_{\mathrm{n}})} \tag{18}$$

3. Particle Scattering Factor

The well-known equation of Debye for the particle scattering factor[26,27] is normally rewritten for a chain molecule of x units as

$$P(\vartheta) = \frac{1}{x^2}\sum_{(i,j)} \phi_{ij} \tag{19}$$

where

$$\phi_{ij} = \langle \sin (sr_{ij})/sr_{ij} \rangle \tag{20}$$

with

$$s = 4\pi/\lambda \sin (\vartheta/2) \tag{21}$$

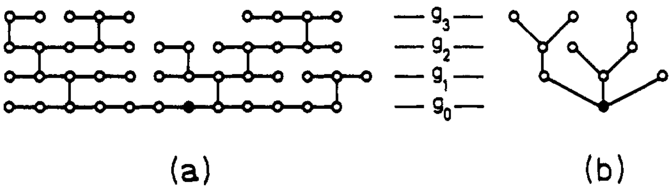

Figure 1. Part a is the representation of vulcanisates as trees. Part b is obtained by the elementary contraction of part a.

Here ϑ is the scattering angle, λ the wavelength of the incident beam, r_{ij} the distance between the centers of two repeat units i and j. The atomic shape factors for each repeat unit are assumed to be constant and, since each repeat unit has been approximated by a point, they are here made equal to unity. The angled brackets in eq 20 denote the configurational average, so that ϕ_{ij} is actually the Fourier transform of the configurational distribution in time with respect to s. For polydisperse systems the observable, z-average particle scattering factor is

$$P_z(\vartheta) = \sum_{n=0}^{\infty} \langle N_{\mathrm{n}} \rangle_{\mathrm{w}} \phi(n)/DP_{\mathrm{w}} \tag{22}$$

where the coefficient $\langle N_{\mathrm{n}} \rangle_{\mathrm{w}}$ denotes the weight-average number of paths of length n ($= |i - j|$). The Fourier transform for a Gaussian distribution is given by

$$\phi_{ij} = \exp(-s^2\langle r_{ij}^2 \rangle/6) \tag{23}$$

with

$$\langle r_{ij}^2 \rangle = b^2 n_{ij} \tag{24}$$

where n_{ij} is the number of links between repeat units i and j, and b^2 the mean-square distance between two adjacent repeat units. Thus eq 10 is valid and the particle scattering factor for vulcanisates with Gaussian subchains is simply given by eq 13

$$DP_{\mathrm{w}}P_z(\vartheta) = (1 + \alpha\phi)\bar{f}_{\mathrm{w}}(\phi)/[1 - (\bar{f}_{\mathrm{w}}(\phi) - 1)\alpha\phi] \tag{25}$$

where ϕ is defined by

$$\phi = \exp(-u) = \exp(-s^2b^2/6) \tag{26}$$

and s is given by eq 21. (For a random flight model,[28] ϕ is defined by $\phi = \sin (sb)/sb$.) The function $\bar{f}_{\mathrm{w}}(\phi)$ in eq 25 is the particle scattering factor for a primary linear chain, first given by Debye for a monodisperse system.[27,29] The z-average radius of gyration is always found from $(\partial P_z(\vartheta)/\partial u)_{u=0}$, thus

$$\langle S^2 \rangle_z = \frac{b^2}{6}\,\frac{(1 + \alpha)^2(\bar{y}_z - \bar{y}_{\mathrm{w}}^{-1}) + 3\alpha\bar{y}_{\mathrm{w}}}{(1 + \alpha)\{1 - \alpha(\bar{y}_{\mathrm{w}} - 1)\}} \tag{27}$$

which reduces in good approximation (for $\bar{y}_{\mathrm{w}} > 100$) to

$$\langle S^2 \rangle_z = (b^2/6)(\bar{y}_z/\bar{y}_{\mathrm{w}})DP_{\mathrm{w}} \tag{27'}$$

The ratio $\langle S^2 \rangle_z/DP_{\mathrm{w}}$ depends only on the primary chain distribution. However, as often observed, especially for comb-shaped systems,[30,31] the actual unperturbed dimensions are much bigger than that predicted by theory based on a random-flight model.[2,3,32] There have even been some reports of a decrease of the Θ temperature by branching,[33,34] although estimation of the Θ temperature from the light-scattering second virial coefficient becomes more and more difficult because of its smaller value[15] and smaller temperature dependence.[31] It is reasonable to assume that branching will affect the chain dimension near the Θ temperature and the random-flight model with the same parameters as in the corresponding linear system

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(23) K. Kajiwara, *Polymer*, **12**, 57 (1971).
(24) G. V. Schulz, *Z. Phys. Chem.*, **B43**, 25 (1939).
(25) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
(26) P. Debye, *Ann. Phys.*, **46**, 809 (1915).
(27) P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).
(28) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).
(29) For sufficiently small u, eq A11 reduces to the well-known Debye's formula[27]

$$B_0(u;y) = (2/yu^2)[yu - 1 + \phi^y]$$

(30) I. Noda, T. Horikawa, T. Kato, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 795 (1970).
(31) G. C. Berry, *J. Polym. Sci., Part A-2*, **9**, 687 (1971).
(32) E. F. Casassa and G. C. Berry, *J. Polym. Sci. Part A-2*, **4**, 881 (1966).
(33) M. Wales and H. Coll, *Ann. N. Y. Acad. Sci.*, **164**, 41 (1969).
(34) F. Candau and F. Funka, *Makromol. Chem.*, **149**, 41 (1971).

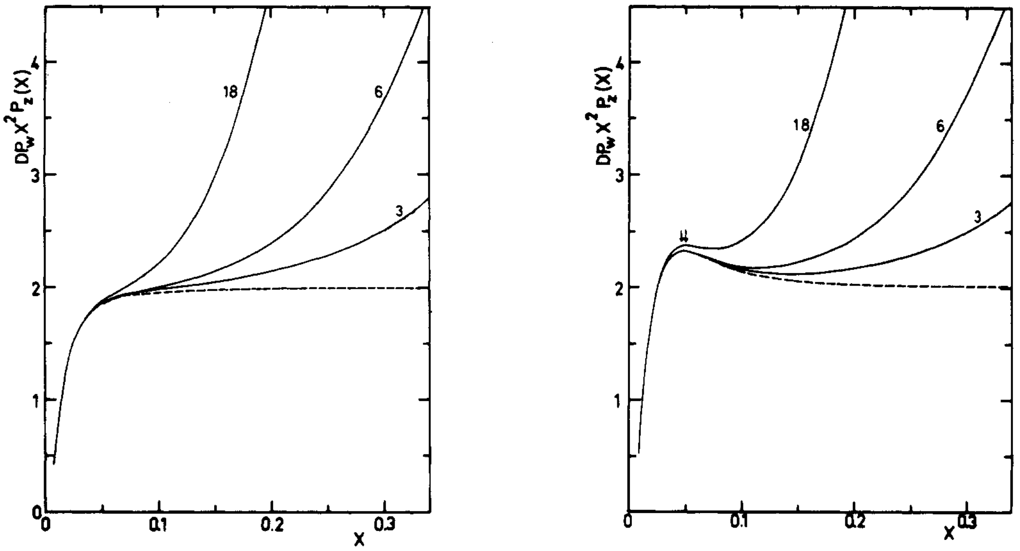

Figure 2. Kratky plots of stiff vulcanisates as a function of $X = as$. The numbers in the figures denote the value of a/b. The dashed curves show the Kratky plots of vulcanisates of Gaussian subchains. (a/b = 1.) All curves are calculated for $\alpha = 9.008 \times 10^{-4}$ and $DP_w = 10^4$. (a, left) Vulcanisates with monodisperse primary chains. The solid arrow indicates the location of maxima in the plots, except that in the case of a/b = 10 this maximum is shifted, as indicated by the dashed arrow. (b, right) Vulcanisates with most probable primary chain distributions.

will fail to give a correct unperturbed dimensions. A greater segment density around the branch nodes causes chain expansion, so that the unusual chain expansion in branched systems is, at least at the Θ temperature, due more to short-range than long-range interactions. For submolecular scattering ($s^2\langle S^2\rangle > 3$),[35] short-range interactions have a dominant effect on the particle scattering factor which results in significant deviations from Debye's expression,[27] based on the Gaussian segment distribution, even though Debye's expression is valid for almost all cases of molecular scattering ($s^2\langle S^2\rangle < 3$),[36,37] including branched system.[31] On the other hand, long-range interactions have a minor effect on the form of the particle scattering factor in the vicinity of the Θ temperature.[38,39]

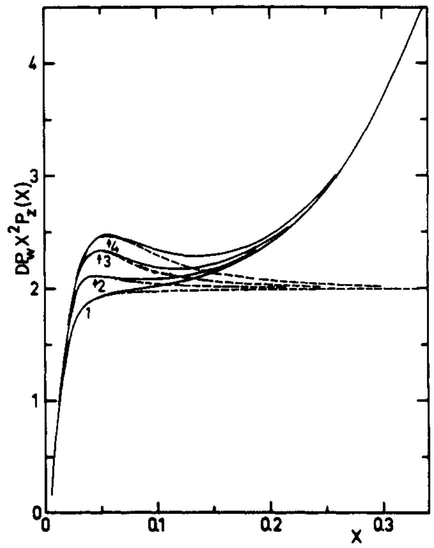

Figure 3. Kratky plots for vulcanisates ($DP_w = 10^4$) with differing monodisperse primary chain lengths. Curve 1 for $\alpha = 0$ (no cross-links), curve 2 for $\alpha = 3.001 \times 10^{-4}$, curve 3 for $\alpha = 9.008 \times 10^{-4}$, and curve 4 for $\alpha = 1.904 \times 10^{-3}$. The arrows indicate the maxima for each curve except curve 1 (where no maximum was observed). Solid curves are calculated for a/b = 6 and dashed curves for a/b = 1 (Gaussian subchain).

Although there is no theory available which treats short-range interactions due to high segment densities about branched nodes, it will be approximately treated here as a kind of chain stiffness regarded as a function of both chain structure and branching density. There are two types of theories proposed to handle local chain stiffness: (a) in mechanical models[40-44] and (b) statistical models.[45-48]. In (a) bending and/or torsional potentials are applied to the Hookean tensile springs of the Rouse model;[44] whereas in (b) chain stiffness is taken into account as a spatial correlation between two neighboring steps. Harris and Hearst[49] showed that (a) and (b) are equivalent formulations for calculating the mean-square distance and henceforward attention is confined to statistical models. Following the worm-like model theory developed by Daniels,[47] the Fourier transform of the segment distribution function is given by

$$\phi_{ij} = \left\{1 + \frac{1}{3}a^2s^2 - \frac{11}{135}a^3ts^4 + \frac{107}{405}a^4s^4\right\} \exp\left(-\frac{1}{3}ats^2\right) \tag{28}$$

with contour length $t = |i - j|b$, and the Kratky-Porod persistence length a.[45] Equation 28 is equivalent to the Nagai-Flory procedure of expressing the Fourier transform as an expansion based on the Gaussian approximation,[35,50] *i.e.*

$$\phi_{ij} = \exp(-s^2\langle r_{ij}^2\rangle/6)\{1 + g_2(s^2\langle r_{ij}^2\rangle/3) + g_4(s^2\langle r_{ij}^2\rangle/3) + \cdots\} \tag{29}$$

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(35) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

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(48) J. J. Hermans and R. Ullman, *Physica*, **18**, 951 (1952).

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(50) K. Nagai, *J. Chem. Phys.*, **38**, 924 (1963).

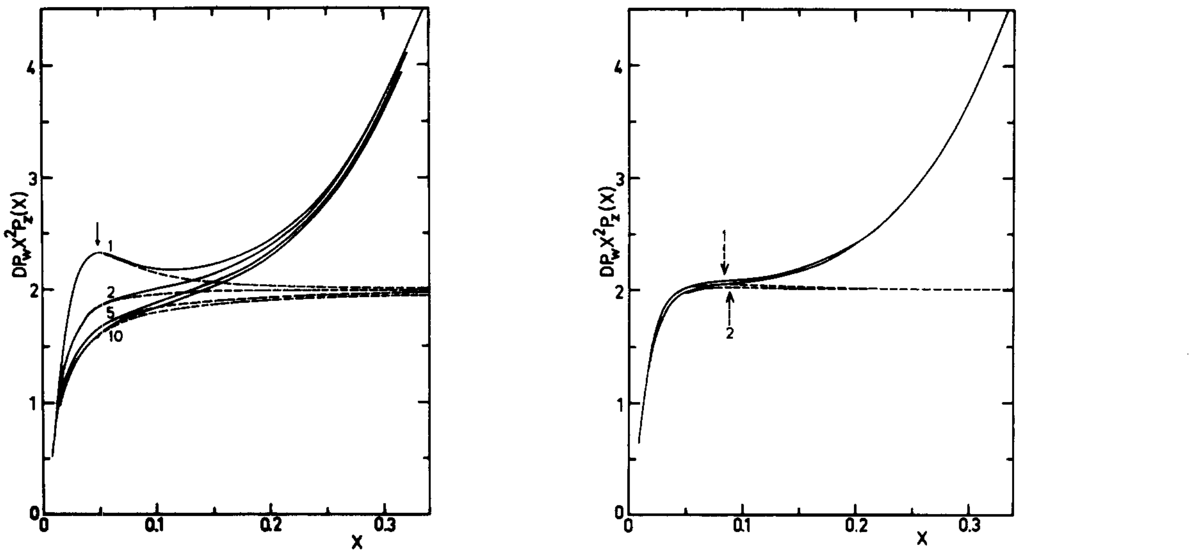

Figure 4. Kratky plots for vulcanisates ($DP_w = 10^4$ and $\alpha = 9.008 \times 10^{-4}$) with different primary chain distributions. Solid curves for $a/b = 6$ and dashed curves for $a/b = 1$. (a) The numbers in the figure denote the value of $\bar{y}_w/\bar{y}_n$. The maximum (arrow) is observed only for the case of a monodisperse primary chain distribution. (b) Curve 1 for the vulcanisate of an equimolar mixture of two monodisperse primary chains of $y = 500$ and 1500. Curve 2 for $\bar{y}_w/\bar{y}_n = 1.5$. For stiff chains no maximum is observed. The dashed arrows show the location of maxima for vulcanisates with Gaussian subchains.

where

$$g_2 = 0$$

$$g_4 = -\frac{1}{8}\left(1 - \frac{3\langle r_{ij}^4\rangle}{5\langle r_{ij}^2\rangle^2}\right)\text{etc.} \qquad (30)$$

Equation 29 is generally valid, but because of truncation errors eq 28 can be applied only when $|i - j| \gg 1$. Equation 29 is useful for estimating the truncation error, using values of $\langle r_{ij}^2\rangle$, $\langle r_{ij}^4\rangle$, etc., cited by various authors.[51] On introducing eq 28 into eq 13, the particle scattering factor is found to be

$$DP_wP_z(\vartheta) = DP_w\left(1 + \frac{1}{3}a^2s^2 + \frac{107}{405}a^4s^4\right)P_z^0(\vartheta) - \frac{11}{135}a^3bs^4\phi\left[\frac{\alpha\{\bar{f}_w(\phi)\}^2 + (1 + \alpha\phi)\bar{f}_w'(\phi)}{\{1 - (\bar{f}_w(\phi) - 1)\alpha\phi\}^2}\right] \qquad (31)$$

Here $P_z^0(\vartheta)$ is the particle scattering factor for a Gaussian subchain model given by eq 25 and ϕ is defined in terms of the persistence length a by a modified form of eq 26

$$\phi = \exp(-u) = \exp(-(1/3)abs^2) \qquad (32)$$

Finally, the derivative $\bar{f}_w'(\phi)$ is evaluated from eq 17

$$\bar{f}_w'(\phi) = \frac{2}{(1 - \phi)^2} - \frac{2(1 + \phi)}{(1 - \phi)^3\bar{y}_n}[1 - N(\phi)] + \frac{2}{(1 - \phi)^2}W(\phi) \qquad (33)$$

Figures 2–4 show the particle scattering factors of randomly cross-linked systems with monodisperse and most probably distribution primary chains. The z-average radius of gyration for this model is again found from $(\partial P_z(\vartheta)/\partial u)_{u=0}$, thus

$$\langle S^2\rangle_z = \frac{ab}{3}\frac{(1 + \alpha)^2(\bar{y}_z - \bar{y}_w^{-1}) + 3\alpha\bar{y}_w}{(1 + \alpha)\{1 - \alpha(\bar{y}_w - 1)\}} - a^2 \qquad (27'')$$

Benoit's asymptote of the particle scattering factor[52,53] often provides a convenient characterization for polydispersity. The function $\bar{f}_w(\phi)$ has an asymptote

$$\bar{f}_w(\phi) = \frac{2}{u}\left(1 - \frac{1}{\bar{y}_nu}\right) \qquad (A11')$$

so that the asymptotic form found of eq 25, for high u, is

$$P(\vartheta)^{-1} = (1/2)DP_w(1 + 3\alpha)u + (1/2)DP_w \times [1 - (2\bar{y}_n - 1)\alpha]/\bar{y}_n \qquad (34)$$

and is valid even for stiff branched systems in an appropriate range of u.[54] Benoit's asymptotic extrapolation procedure for obtaining a measure of polydispersity, is illustrated in Figure 5. Equation 34 reduces to Benoit's equation for the asymptote[52] when $\alpha = 0$.

4. Weight-Average Mean-Square Radius of Gyration

It is often required to calculate the weight-average mean-square radius of gyration instead of the experimentally observed z average. The principal tool for this calculation is the bivariate gf introduced in a previous paper.[15] The univariate pwgf (see section 2) is readily extended to the bivariate gf with dummy variables θ_1, θ_2 (collectively denoted by the set $\{\theta\}$):

$$u_0(\{\theta\}) = \sum_{y_0=1}^{\infty}m_{y_0}\theta_1^{y_0}\theta_2^{B_0(\phi;\,y_0)}(1 - \alpha + \alpha u_1(\{\theta\}))^{y_0} \qquad (8')$$

$$u_i(\{\theta\}) = \sum_{y_i=1}^{\infty}m_{y_i}\theta_1^{y_i}\theta_2^{B_i(\phi;\,y_0,\,y_1,\,\cdots,\,y_i)}(1 - \alpha + \alpha u_{i+1}(\{\theta\}))^{y_i-1} \qquad (i \geq 1) \quad (9')$$

each of which is a simple convolution of the weight fraction gf and the univariate pwgf for appropriate generations. The corresponding enumeration gf, given by the dif-

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(51) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **50**, 4178 (1969); see also ref 34.

(52) H. Benoit, *J. Polym. Sci.*, 11, 506 (1953).

(53) H. Benoit, A. M. Holtzer, and P. Doty, *J. Phys. Chem.*, **58**, 635 (1954).

(54) For a stiff branched system, an asymptote is written as

$$P_z(\vartheta)^{-1} = (1/2)DP_w\left[(1 + 3a) - \frac{1}{3}\left(\frac{a}{b}\right) \times \left\{1 - \frac{11}{45}(1 + 2\alpha)\right\}\{1 - (2\bar{y}_n - 1)\alpha\}/\bar{y}_n\right]u + \frac{DP_w}{2\bar{y}_n}[1 - (2\bar{y}_n - 1)\alpha] \qquad (34')$$

ferentiation of eq 8′ with respect to θ_2 at $\theta_2 = 1$, includes the additional dummy variable θ_1 which stores genetic information relating to the size of trees in a clone

$$E(\theta_1,\phi) = \Sigma m_y \theta_1{}^y B_0(\phi;y)(1 - \alpha + \alpha u)^y + \frac{\alpha\phi[\Sigma m_y \theta_1{}^y B_0(\phi;y)(1 - \alpha + \alpha u)^{y-1}]^2}{1 - \alpha\phi[\Sigma m_y \theta_1{}^y \{B_0(\phi;y) - 1\}(1 - \alpha + \alpha u)^{y-2}]} \quad (35)$$

where u is the abbreviation for $u_1(\theta_1,1)$, $u_2(\theta_1,1)$, . . . , etc. As in ref 15, integration or differentiation of eq 35 with respect to θ_1 yields the desired enumeration gf for differently weighted averages. To calculate the weight-average mean-square radius of gyration, for example, we need to integrate eq 35 with respect to θ_1. This is achieved by replacing the variable θ_1 by a new variable ξ defined thus

$$\xi = \theta_1(1 - \alpha + \alpha u) \quad (36)$$

which allows eq 35 to be rewritten in the form:

$$E(\xi,\phi) = B(\xi,\phi) + \frac{\alpha\phi[B(\xi,\phi)]^2}{\left[\dfrac{2\alpha W(\xi)}{-(1 - \alpha) + \sqrt{(1 - \alpha)^2 + 4\alpha W(\xi)}}\right]^2 - \alpha\phi[B(\xi,\phi) - W(\xi)]} \quad (37)$$

where

$$B(\xi,\phi) = \frac{1 + \phi}{1 - \phi}W(\xi) - \frac{2\phi}{(1 - \phi)^2 \bar{y}_n}[N(\xi) - N(\phi\xi)] \quad (38)$$

The enumeration gf suitable for calculating the weight-average mean-square radius of gyration is now obtained by integrating eq 37

$$\int_0^1 \frac{1}{\theta_1} E(\xi,\phi)\mathrm{d}\theta_1 = \int_0^1 E(\xi,\phi)(2\xi)^{-1} \times \left\{\frac{(1 - \alpha)\bar{y}_w}{\sqrt{(1 - \alpha)^2 + 4\alpha W(\xi)}} - (\bar{y}_w - 2)\right\}\mathrm{d}\xi \quad (39)$$

When $\alpha < 1$, the term including $W(\xi)$ and ξ is well approximated in the range $0 < \xi < 1$ by

$$\frac{2\alpha W(\xi)}{-(1 - \alpha) + \sqrt{(1 - \alpha)^2 + 4\alpha W(\xi)}} \simeq 1 \quad (40)$$

The weight-average mean-square radius of gyration is obtained by differentiating eq 39 with respect to ϕ at $\phi = 1$, thus the final result is

$$\langle S^2\rangle_w \simeq \frac{b^2}{12}\bar{y}_w \int_0^1 \frac{Z'(\xi)}{(1 - \alpha\bar{y}_w Z(\xi))^2} \times \left\{\frac{(1 - \alpha)\bar{y}_w}{\sqrt{(1 - \alpha)^2 + 4\alpha W(\xi)}} - (\bar{y}_w - 2)\right\}\alpha\xi \quad (41)$$

where $Z(\xi)$ is the z-fraction gf defined by

$$Z(\xi) = \xi W'(\xi)/\bar{y}_w \quad (42)$$

For monodisperse primary chains eq 41 reduces to the result

$$\langle S^2\rangle_w = \frac{b^2(1 - \alpha)}{\alpha}\left(\frac{y}{4 + (1 - \alpha)^2 y}\right)^{3/2} \times \ln\left(\frac{\sqrt{y(4 + (1 - \alpha)^2 y)} + (1 + \alpha)y}{\sqrt{y(4 + (1 - \alpha)^2 y)} - (1 + \alpha)y} \times \frac{\sqrt{y(4 + (1 - \alpha)^2 y)} - (1 - \alpha)y}{\sqrt{y(4 + (1 - \alpha)^2 y)} + (1 - \alpha)y}\right) \quad (41')$$

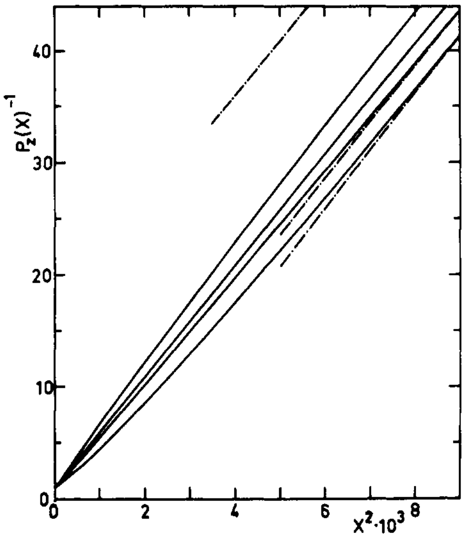

Figure 5. Zimm plots and Benoit's asymptotes of vulcanisates ($DP_w = 10^4$, $\alpha = 9.008 \times 10^{-4}$ and $a/b = 6$) with different primary chain distributions. The solid curves show Zimm plots for vulcanisates with $\bar{y}_w/\bar{y}_n = 5$, $\bar{y}_w/\bar{y}_n = 2$, $\bar{y}_w/\bar{y}_n = 1.5$, and $\bar{y}_w/\bar{y}_n = 1$ (from the top). The chained lines show Benoit's asymptotes of these Zimm plots. In the case of $\bar{y}_w/\bar{y}_n = 2$ (the most probable primary chain distribution), Benoit's asymptote overlaps with the corresponding Zimm plot.

5. Discussion

The use of eq 28 implies the approximation that $\langle r_{ij}{}^2\rangle$ is proportional to $|i - j|$, which is acceptable only for long chains. However, this approximation will be valid for submolecular scattering in the range corresponding to Bragg distances larger than 100 ~ 150 Å,[55] which corresponds, in the case of $a/b = 6$, to $X < 0.2$, where $X \equiv as$. Although the convergence of all scattering envelopes to a common curve at large X values suggests that the persistence length will be determined uniquely regardless of branching densities, it is beyond the scope of the present theory to determine the transition point. It has been suggested that the branch size may be determined from the location of maxima in Kratky plots[56] (indicated by arrows in Figures 2, 3, and 4 where applicable). However, this conjecture is no longer valid when the primary chain distribution is broader than that of the most probable distribution ($\bar{y}_w/\bar{y}_n = 2$). Further for narrower primary chain distributions, the maximum is shifted and becomes obscure as a result of increasing chain stiffness (*cf.* Figure 4b).

The shape of scattering envelopes is very sensitive to the primary chain distribution (see Figure 4). For a most probable primary chain distribution there is no difference between the particle scattering factor of a branched system and that of a linear system of the same weight-average degree of polymerization, except for extremely large α values. It is not advisable to use Benoit's asymptote for stiff branched systems of broad primary chain distributions, because the contribution from the second term in eq 31 is not negligible when eq A11″ is valid (*cf.* Figure 5).

As reported by Kilb,[57] the z-average radius of gyration reduces to the simple form of eq 27′. The weight-average radius of gyration does not generally give a simple form. Zimm and Stockmayer's model for heterogeneous systems[1] corresponds to randomly cross-linked chains of most

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(55) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 280 (1970).
(56) B. A. Fedorov, *Vysokomol. Soedin., Ser. A*, **12**, 816 (1970).
(57) R. W. Kilb, *J. Polym. Sci.*, **38**, 403 (1959).

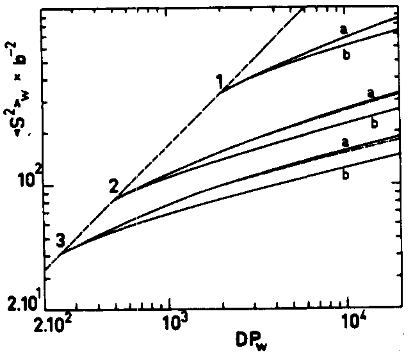

Figure 6. The weight-average radii of gyration of vulcanisates with two different primary chain distributions. (Curves a for monodisperse primary chains and curves b for most probable primary chain distributions). Curves 1 for $\bar{y}_w = 2000$, curves 2 for $\bar{y}_w = 500$, and curves 3 for $\bar{y}_w = 250$. The dashed line shows the weight-average radius of gyration of a linear system. The chained curves are calculated by eq 43.

probable primary chain distributions. According to them, the weight-average radius of gyration is given by

$$\langle S^2\rangle_w = (b^2/6n_w)DP_w \ln (1 + n_w) \qquad (43)$$

where n_w is the weight-average number of branch units per molecule, given by

$$n_w = \bar{y}_w/(1 - \alpha\bar{y}_w) \qquad (44)$$

Subsequently Gordon and Malcolm recovered eq 43 from a quite different approach.[13] As shown in Figure 4, Zimm and Stockmayer's formula agrees well with the present calculations for systems of monodisperse primary chains, but not those of most probable primary chain distributions. The weight-average radii of gyration of the latter have lower values than those calculated by eq 43. When eq 43 is assumed *a priori*, the weight-average number of branch units per molecule will be overestimated in the most probable system as was observed by Kamada and Sato.[58] The curves in Figure 6 are, however, well approximated by eq 43 when the apparent weight-average number of branch units per molecule n_w' is written in the form

$$n_w' = \Upsilon n_w \qquad (45)$$

where the parameter Υ depends only on the primary chain distribution, with $\Upsilon \approx 1$ for monodisperse primary chains and $\Upsilon \approx 1.3$ for most probable primary chain distributions. The difference between the results of Zimm and Stockmayer (and also of Gordon and Malcolm) and those of the present study result from the approximations introduced in those calculations (see eq B21 in ref 1 and eq 102 in ref 13). As would be expected, these approximations become prohibitively serious as the length of the primary chains is decreased or as the fraction of cross-links per primary chains, α, is increased.

Acknowledgment. We are indebted to Professor W. Burchard for his encouragement and also Professor M. Gordon and Messrs S. Ross-Murphy and J. W. Kennedy for valuable comments during the course of this work. The work was supported by Deutsche Forschungsgemeinschaft and the Gulbenkian Foundation.

Appendix

The enumeration generating function $B_i(\phi;y_0,y_1,\ldots,y_i)$ is rederived in this appendix by an *ad hoc* combinatorial argument avoided in a previous paper.[17] We assume an equal probability of forming cross-links for all monomer units in chains, so that the problem reduces to merely counting the number of ways in which a linear succession of n links may be obtained by taking an arbitrary number of links from each primary chain from the zeroth to the ith generation. Thus, a linear sequence of n links takes n_0 links from the zeroth generation, n_1 links from 1st generation etc., so that

$$n = \sum_{s=0}^{i} n_s + i \qquad (A1)$$

where the enumeration of cross-links is included. There are $2(y_s - n_s)$ ways if $n_s \neq 0$ and y_s ways if $n_s = 0$ to take n_s links from the sth generation, and the probability of picking up n_s links from the sth generation is given by

$$\begin{aligned} p_s(n_s) &= 2(y_s - n_s)/y_s^2 && \text{if } n_s > 0 \\ p_s(0) &= 0 && \text{if } n_s = 0 \end{aligned} \qquad (A2)$$

for the zero-th and the ith generation and

$$\begin{aligned} p_s(n_s) &= 2(y_s - n_s)/y_s(y_s - 1) && \text{if } n_s > 0 \\ p_s(0) &= 0 && \text{if } n_s = 0 \end{aligned} \qquad (A3)$$

for other (intermediate) generations, where y_s denotes the degree of polymerization of the primary chain on the sth generation. The probability that the arbitrary chosen path (linear succession), starting at a repeat unit on g_0 and terminating on some unit on g_i, has the total length n is

$$P_i(n) = \Sigma \prod_{s=0}^{i} p_s(n_s) \qquad (A4)$$

where the summation is taken over all combinations of n_s's with the condition given by eq A1. As there are y_0y_i distinct paths any of the y_0 units on g_0 terminates at any of the y_i units on g_i, the mean number $A_i(n)$ of these paths of total length n per root in the clone will be given by

$$A_i(n) \equiv \zeta(\phi^n)B_i(\phi; y_0, y_1, \cdots, y_i = y_0y_iP_i(n) \qquad (A5)$$

By rewriting eq A2 and A3 with the dummy variable ϕ

$$\begin{aligned} p_0(n_0,\phi) &= 2(y_0 - n_0)\phi^{n_0}/y_0^2 \qquad n_0 > 0 \\ p_0(0,\phi) &= 1/y_0 \end{aligned} \qquad (A6)$$

$$\begin{aligned} p_i(n_i,\phi) &= 2(y_i - n_i)\phi^{n_i+1}/y_i^2 \qquad n_i > 0 \\ p_i(0,\phi) &= \phi/y_i \end{aligned} \qquad (A7)$$

$$p_s(n_s,\phi) = 2(y_s - n_s)\phi^{n_s+1}/y_s(y_s + 1)$$

$$0 < s < i \text{ and } n_s > 0 \qquad (A8)$$

then the enumeration generating function $B_i(\phi;y_0,y_1,\ldots,y_i)$ is found to be

$$B_i(\phi; y_0, y_1, \cdots, y_i) = y_0y_i\sum_{n_0=1}^{\infty}\sum_{n_1=1}^{\infty}\cdots\sum_{n_i=1}^{\infty}\prod_{s=0}^{i}P_s(n_s,\phi) =$$

$$y_0y_i\left[\frac{1}{y_0^2}\left\{\frac{y_0(1 + \phi)}{(1 - \phi)} - \frac{2\phi(1 - \phi^{y_0})}{(1 - \phi)^2}\right\}\right] \times$$

$$\left[\frac{\phi}{y_i^2}\left\{\frac{y_i(1 + \phi)}{(1 - \phi)} - \frac{2\phi(1 - \phi^{y_i})}{(1 - \phi)^2}\right\}\right] \times$$

$$\prod_{s=1}^{i-1}\frac{\phi}{y_s(y_s - 1)}\left\{\frac{y_s(1 + \phi)}{(1 - \phi)} - \frac{2\phi(1 - \phi^{y_s})}{(1 - \phi)^2} - y_s\right\} \qquad (A9)$$

For the enumeration generating function in ensemble 2, the factor y_0 should be omitted in eq A9 because a repeat unit is taken as a root (not a whole primary chain). A path is always assumed to start from that chosen root. Apparently eq A9 reduces to a product of $i + 1$ simpler

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(58) K. Kamada and H. Sato, *Polym. J.*, **2**, 489 (1971).

generating functions times ϕ^i

$$B_i(\phi; y_0, y_1, \cdots, y_i) = \phi^i[B_0(\phi; y_0)][B_0(\phi; y_i)]\prod_{s=1}^{i-1}[B_0(\phi; y_s) - 1]/(y_s - 1) \qquad i > 1 \quad \text{(A10)}$$

where

$$B_0(\phi; y) = \frac{1}{y}\left[\frac{y(1 + \phi)}{1 - \phi} + \frac{2\phi(1 - \phi^y)}{(1 - \phi)^2}\right] \quad \text{(A11)}$$

is the enumeration generating function of the number of paths of length n for an unvulcanized primary chain.

Intrinsic Viscosity of Wormlike Chains. Determination of the Shift Factor

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Received October 3, 1973

ABSTRACT: The intrinsic viscosity of stiff chains without excluded volume is evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to wormlike cylinder models in the same spirit as that of the Yamakawa–Fujii theory of the translational friction coefficient. The molecular parameters involved are only the chain contour length L, the Kuhn segment length λ^{-1}, and the molecular diameter d. The final results are obtained only numerically by the use of a digital computer, but the semiempirical analytical expressions, which are very accurate, are presented for practical use. A method of determining a shift factor defined by $M_L = M/L$ with M the molecular weight is proposed, based on an analysis of intrinsic viscosities in conjunction with sedimentation coefficients. It is applied to DNA, poly(n-butyl isocyanate), and cellulose nitrate. It is concluded that the values of M_L determined for the latter two polymers are close to those corresponding to the all-trans conformation.

Analysis of the conformational and transport properties of stiff chain macromolecules has often been made on the basis of a continuous wormlike-chain model.[1] In doing this, however, a difficulty arises from the fact that the model chain is characterized by the contour length L and the Kuhn statistical segment length λ^{-1}, or the persistence length $(2\lambda)^{-1}$, while the relationship between L and the molecular weight M is not generally known except for molecules having rigid local conformations such as DNA and ladder polymers. We may define a shift factor M_L or f as the proportionality constant between L and M or the number n of bonds in the spine of the chain by[2,3]

$$M = M_L L \quad (1)$$

$$n = fL\lambda \quad (2)$$

In the case of flexible chains, values of the mean-square radius $\langle S^2\rangle$ are determined as a function of M if the characteristic ratio[4] is determined, whereas in the application of the wormlike-chain model to stiff chains, values of $\langle S^2\rangle$ as a function of M cannot be predicted unless proper values are assigned to both M_L and λ.[5] In many cases, once the value of M_L has been given, the determination of λ is not difficult.

For short broken chains of polymethylene, poly(oxymethylene), and the like (with a few exceptions), Maeda, Saito, and Stockmayer[3,6] have concluded that the best shift factor f may be obtained by taking L as the length of the chain fully extended to the all-trans conformation, based on a comparison of the second and fourth moments of the end-to-end distance of the broken and wormlike chains. However, there has not yet been established a method of determining the shift factor M_L from experiment. Thus, in the present paper, we propose a method for doing this, based on an analysis of intrinsic viscosities in conjunction with sedimentation coefficients. For this purpose, we first develop a theory of the intrinsic viscosity of wormlike chains in the same spirit as in the previous paper on the translational friction coefficient.[7]

The theory is developed by an application of the Oseen–Burgers procedure[8,9] of hydrodynamics to the wormlike cylinder model, and its formulation is given in section I. The discussion of this procedure in comparison with the Kirkwood procedure[10,11] and also the related references are given in detail in the previous paper,[7] and not repeated herein. However, we emphasize that our theories of the intrinsic viscosity and the sedimentation coefficient are consistent to be combined. Although such a consistent pair of theories for the two transport properties has also been presented by Ullman,[12] his theory is based on the wormlike-bead model with the use of the Kirkwood procedure, followed by the limiting process, and involves one more parameter than ours. In section II, numerical solutions of the derived integral equation, which cannot be solved analytically, are given, and in section III, the results are used to analyze the viscosity data for DNA. In section IV, we propose a method of determining M_L and apply it to DNA and several other stiff macromolecules.

I. Formulation

For convenience, all lengths are measured in units of the Kuhn segment length λ^{-1}, so that the unreduced con-

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