Application of the Cascade Theory to Calculation of Particle Scattering Factors of Polydisperse Systems of Stiff Chains

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ABSTRACT: The mean-square radii of gyration $\langle S^2\rangle_z$ and the particle scattering factors $P_z(\Theta)$ of polydisperse ($M_w/M_n = 2$) stiff linear chains, the weight-average molecular weights, and the weight distributions were calculated applying the cascade theory of Good and of Gordon. Making use of the well-known result of Schulz that polydispersity is decreased by chain coupling, the mentioned averages were derived for lower degrees of polydispersity ($M_w/M_n < 2$). Relatively simple analytic expressions were obtained even when chain stiffness was taken into account. *Increasing* chain stiffness and *decreasing* polydispersity both cause similar deviations of the mean-square radius of gyration from the Gaussian behavior at a low degree of polymerization DP_w. Thus, according to the properties of the mean-square radii of gyration, polydisperse chains seem to have a *lower* chain stiffness than the chains have in reality. Conversely, *increasing* chain stiffness and *increasing* polydispersity cause a similar downturn of the reciprocal particle scattering factor at large angles. Therefore polydisperse chains give indications of a *higher* chain stiffness, if the angular dependence of the scattered light is analyzed.

1. Introduction

In the course of our theoretical studies on branched polymers the correlation between molecular weight distribution and conformation of linear and branched macromolecules appeared to us to be of particular interest. As is well known, polymerization of linear chains results in a more or less broad molecular weight distribution depending on the kinetic mechanism.[1-4] Furthermore, decreasing molecular heterogeneity is achieved by multiple coupling of chains.[5,6] While the mechanism of chain coupling has no influence on the width of the molecular distribution, it certainly affects the conformation of the macromolecules. To give an example, the molecules of head-to-tail coupled linear chains will exhibit more extended coil dimensions than the corresponding star-like polymers, whose primary chains are coupled at one point. The purpose of this paper is the calculation of conformational z-averages of the mean-square radius of gyration $\langle S^2\rangle_z$ and the particle scattering factor $P_z(\Theta)$, as well as the already-known molecular weight averages M_w and M_n.

While the molecular weight averages can be calculated by applying the simple convolution principle, a more involved statistical method is required for the calculation of the conformational averages. The cascade theory, developed by Good[7-9] and by Gordon[10-12] for branched polymers, provides a suitable tool for such calculations, also for linear molecules. The essential features of cascade theory is the use of probability generating functions, which by a differentiation operation yield the desired conformational averages. It is of great advantage that these averages are simultaneously performed with respect to a molecular weight distribution.

By combination of existing theories of homodisperse stiff chains[13-19] with the cascade theory the influence of molecular heterogeneity on the scattering behavior of stiff chains is accessible to calculation. For our purpose, Daniels' approach[19] to a solution of the chain stiffness problem is most appropriate, because the resulting Fourier transform of the end-to-end distribution (needed for the calculation of particle scattering factors) can be directly introduced into the cascade theory.

In the following, analytical expressions are derived for the head-to-tail coupling. Details of the calculation for star-like coupling will be given elsewhere.[20]

2. Linear Chains with the Most Probable Chain-Length Distribution

For a better understanding of the method used below the simple case of linear chains with a most probable distribution of the molecular weight ($M_w/M_n = 2$) is treated in detail.

2.1. Principles of Averaging Due to the Cascade Theory. For the calculation of conformational averages the following double sum has to be considered.[21]

$$\langle\phi\rangle = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\phi_{ij} \tag{1}$$

ϕ_{ij} is a weighting function depending on the distances r_{ij} between two chain elements (repeat units) i and j; the angular brackets indicate the corresponding average. If a suffix is added, a further average over a molecular weight distribution is performed.

A simple counting system for the calculation of such double sums is obtained by considering the polymer molecule as a "family" tree or more precisely as a rooted tree where an arbitrary chain element is choosen as a root. Obviously each chain element has the same chance of becoming a root of a tree and thus a full forest of x isomorphic trees has to be considered for a chain consisting of x monomers or chain elements. Similarly, as is done with family trees, different generations can be introduced for these trees, counting the root as the zeroth generation and

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denoting the next neighbors to be in the first, second, etc., generations (see Figure 1).

In general, owing to the conditions of synthesis, polymers are obtained with more or less broad molecular weight distributions. Let $N(x)$ be the frequency distribution of a linear chain of the degree of polymerization x, then the average degree of polymerization is found by taking the average with respect to $xN(x)$, because the whole assembly of trees has to be considered. Therefore the average obtained is the weight-average degree of polymerization DP_w. All further statistical problems are simplified by introducing generating functions[22] instead of using probability distribution functions themselves. Following Gordon[10-12] such generating functions can be calculated from the probabilities of reaction, sometimes called the link probabilities.

The link probability generation function in the zeroth generation for linear chains is given by

$$F_0(\theta) = (1 - \alpha + \alpha\theta)^2 \tag{2}$$

For all subsequent generations (neglecting substitution effects), one has

$$F_n(\theta) = 1 - \alpha + \alpha\theta \tag{3}$$

In eq 2 and 3 the parameter $1 - \alpha$ is the probability that a reactive group has not reacted in the course of a reaction and α is the probability, that it has.

Since for linear chains the root has two functional groups, the link probability generating function is found by the product of the generating functions of these two groups. In all the other generations only one group is left for further reactions. For determination of the "mean structure of the whole tree" the different link generating functions have to be joined. This can be done by a cascade substitution according to Good[7-9]

$$U_0(\theta) = \theta^{\phi_0}F_0\{\theta^{\phi_1}F_1[\theta^{\phi_2}F_2(\cdots)]\} \tag{4}$$

Inserting eq 2 and 3 into eq 4, one obtains

$$\begin{aligned} U_0(\theta) &= \theta^{\phi_0}[1 - \alpha + \alpha U_1(\theta)]^2 \\ U_n(\theta) &= \theta^{\phi_n}[1 - \alpha + \alpha U_{n+1}(\theta)] \end{aligned} \tag{5}$$

where ϕ_n is a weighting function, now dependent on the distance of the units in the nth generation from the root. $U_0(\theta)$ is called the path weighting generating function. Differentiation with respect of θ at $\theta = 1$ yields the averages of the weighting function.

$$U_0'(1) = \phi_0 + 2\alpha\sum_{n=1}^{\infty}\alpha^{n-1}\phi_n \tag{6}$$

2.2 Special Weighting Functions. According to Kajiwara *et al.*[24] averages with physical meaning are obtained by inserting special weighting functions

$$\phi_n = 1 \qquad U_0'(1) = DP_w \tag{7}$$

$$\phi_n = M_0 \qquad U_0'(1) = M_w \tag{8}$$

$$\phi_n = \langle r_n^2\rangle \qquad U_0'(1) = 2DP_w\langle S^2\rangle_z \tag{9}$$

$$\phi_n = \left\langle\frac{\sin hr_n}{hr_n}\right\rangle \qquad U_0'(1) = DP_wP_z(\Theta) \tag{10}$$

where M_0 = the molecular weight of the monomer (repeating unit), M_w = the weight average of the molecular weight of the chain, $\langle S^2\rangle_z$ = the z average of the mean-square radius of gyration, $\langle r_n^2\rangle$ = the mean-square distance between a monomer of the chain in the nth generation and the root; $h = (4\pi/\lambda)\sin\Theta/2$.

$$\left\langle\frac{\sin hr_n}{hr_n}\right\rangle = \int_0^{\infty} W(r_n)\frac{\sin hr_n}{hr_n}4\pi r_n^2 \mathrm{d}r_n \tag{11}$$

Equation 11 is the Fourier transform of the spatial distance distribution $W(r)$, Θ the scattering angle, and λ the wavelength of the light in the medium.

Degree of Polymerization and the Molecular Weight. The weight average of the degree of polymerization and the molecular weight follow from eq 7 and 8 by summing the corresponding infinite series of eq 6

$$DP_w = (1 + \alpha)/(1 - \alpha) \tag{12}$$

$$M_w = M_0[(1 + \alpha)/(1 - \alpha)] \tag{13}$$

Mean-Square Radius of Gyration. For the calculation of the mean-square radius of gyration $\langle S^2\rangle_z$ and of the particle scattering factor $P_z(\Theta)$ a relationship is required, on the one hand, between the distances $\langle r_n\rangle$, and, on the other hand, the bond length b, the valence angle γ, and the number of repeat units n.

According to Eyring[25] the following relationship holds for the end-to-end distance of the freely rotating chain with a fixed valence angle

$$\langle r_n^2\rangle = b^2\left[\frac{1 + \cos\gamma}{1 - \cos\gamma}n - \frac{2\cos\gamma}{(1 - \cos\gamma)^2}(1 - \cos^n\gamma)\right] \tag{14}$$

Equation 14 is valid for flexible chains ($\cos\gamma = 0$) as well as for stiff ones ($\cos\gamma > 0$). The stiffness of a chain can be characterized by either the persistence length as introduced by Porod[26,27]

$$a = b/(1 - \cos\gamma) \tag{15}$$

or by a reduced parameter q

$$q = b/a = 1 - \cos\gamma \tag{15'}$$

For very long chains ($n \gg 1$, Gaussian region), eq 14 simplifies to

$$\begin{aligned} \langle r_n^2\rangle &= b^2[(1 + \cos\gamma)/(1 - \cos\gamma)]n \\ &= b^2[(2 - q)/q]n = b_{\mathrm{eff}}^2 n \end{aligned} \tag{16'}$$

Using the effective bond length b_{eff} (eq 16′) and the chain stiffness parameter q, eq 14 takes on the equivalent form

$$\langle r_n^2\rangle = b_{\mathrm{eff}}^2\left[n - 2\frac{1 - q}{q(2 - q)}(1 - (1 - q)^n)\right] \tag{16}$$

Insertion of this relationship in eq 12 and 6 yields the z average of the mean-square radius of gyration

$$\langle S^2\rangle_z = b_{\mathrm{eff}}^2\left[\frac{\alpha}{(1 - \alpha)^2} - \frac{1 - q}{q(2 - q)} \times \left(1 - \frac{1 - \alpha}{1 + \alpha}\,\frac{1 + \alpha(1 - q)}{1 - \alpha(1 - q)}\right)\right] \tag{17}$$

For long chains, *i.e.*, $\alpha \simeq 1$, a Gaussian chain behavior is obtained and eq 17 reduces to

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(22) For definition and properties of generating functions, see W. Feller.[23]

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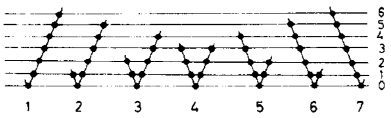

Figure 1. The seven possible rooted trees of a linear heptamer.

$$\langle S^2\rangle_z = b_{\text{eff}}^2[\alpha/(1-\alpha)^2] \qquad (17')$$

The same result may be obtained by inserting eq 16 into eq 6.

Particle Scattering Factor. Up to now the Fourier transform (eq 11) cannot be analytically expressed in terms of structural parameters b and $\cos \gamma$. However, for *long flexible chains* the distance distribution $W(r_n)$ has the well-known form of a Gaussian distribution[12]

$$W(r_n) = \left(\frac{3}{2\pi b_{\text{eff}}^2 n}\right)^{3/2} \exp\left(-\frac{3}{2b_{\text{eff}}^2 n}r_n^2\right) \qquad (18)$$

In this limit the Fourier transform of the spatial distance distribution (see eq 11) is

$$\left\langle\frac{\sin hr_n}{hr_n}\right\rangle = \exp(-\langle r_n^2\rangle h^2/6) = \exp(-X_n^2/6) = Z^n \qquad (19)$$

where $X^2 = h^2 b_{\text{eff}}^2$, $h = (4\pi/\lambda)\sin\Theta/2$, and $Z = \exp(-X^2/6)$. The particle scattering factor of Gaussian chains, obeying the most probable molecular weight distribution, is obtained now from eq 16 and 19.

$$P_z(\Theta) = \frac{1-\alpha}{1+\alpha}\frac{1+\alpha Z}{1-\alpha Z} \qquad (20)$$

The Fourier transform of *stiff chains* was calculated by Daniels[18,19] to a second-order approximation

$$\left\langle\frac{\sin hr_n}{hr_n}\right\rangle = (1 + C_1X^2)Z + C_2X^4\frac{\mathrm{d}}{\mathrm{d}X^2}(Z) \qquad (21)$$

where

$$C_1 = \frac{1}{3}\frac{1-q}{q(2-q)}.$$

$$C_2 = \frac{1}{30}\frac{(22/3) - 6q + q^2}{q(2-q)}$$

For this expression the series in eq 6 can be evaluated analytically resulting in

$$P_z(\Theta) = \frac{1-\alpha}{1+\alpha}\left[(1 + C_1X^2)\frac{1+\alpha Z}{1-\alpha Z} - \frac{1}{3}C_2X^4\frac{\alpha Z}{(1-\alpha Z)^2}\right] \qquad (22)$$

The equations for the degree of polymerization and the molecular weight (eq 12 and 13) agree with those derived by Flory for most probable molecular weight distributions.

Equations 17′ and 20, which describe the conformational averages $\langle S^2\rangle_z$ and $P_z(\Theta)$ for Gaussian chains, are in accord with those for branched polymers,[24] if the special case of bifunctional repeat units is regarded. The analytical expressions for conformational averages of heterodisperse stiff chains (eq 17 and 22) are derived here for the first time.

3. Chain Coupling

3.1. Some General Considerations. As was done in section 2, the statistics of coupled chains can be treated with the aid of the cascade theory. The difference from the simple case discussed before consists in the occurrence of two possibilities of reaction: (a) a monomer can have reacted with the probability α with another monomer building up thereby a primary chain; (b) the monomer could be involved in a coupling reaction with the probability $1 - \alpha$ where a linkage between this monomer and an end group of an already existing primary chain is formed.

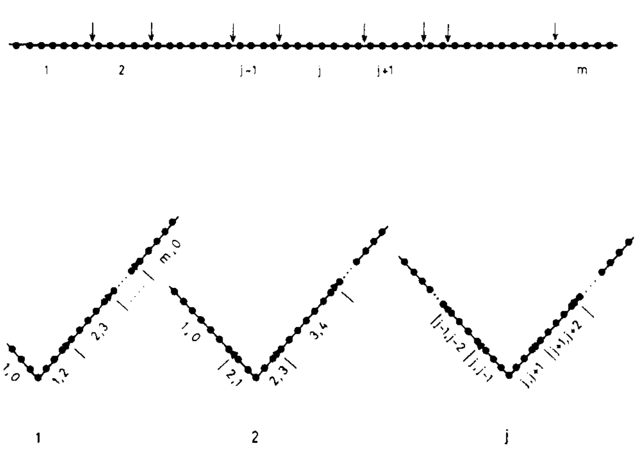

Figure 2. (a, top) Coupling of m primary chains (schematically). The arrows indicate the points of coupling, the figures the number of primary chain. (b, bottom) Three representatives of possible tree structures of the coupled chain. The labeling is as follows. The first number denotes the primary chain considered, the second number the neighbored primary chain or the free end (indicated by the number 0). The numbers beneath the graphs indicate the primary chains the root was chosen from.

Strictly speaking, $1 - \alpha$ indicates the probability of finding an end of a primary chain *before* chain coupling. After chain coupling $(1 - \alpha)p_{i,i+1}$ indicates that a chain end of primary chain i is coupled with probability $p_{i,i+1}$ to primary chain $i + 1$. In the present problem we assume $p_{0,1} = p_{m,0} = 0$ and $p_{i,i+1} = 1$ for all other primary chains. Thus the probability $1 - \alpha$ indicates the likelihood of a coupling reaction between two primary chains, with the exception of the first and last primary chain bound in the macromolecule where $1 - \alpha$ indicates no reaction (free ends). The procedure of calculation is illustrated in Figure 2a,b. Owing to the condition of randomness in the cascade theory, any repeating unit of this coupled chain can become the root of a tree. Depending on the primary chain considered, one has to distinguish between m different groups of tree structures. All trees, the roots of which are monomers of the same primary chain, are collected thereby into one group.

Figure 2b exhibits representatives of trees where either a monomer from primary chain 1, primary chain 2, or primary chain j is choosen as the root. In the first case there are two statistically nonequivalent branches; the branch to the left (in Figure 2b) leads to a free end while the branch to the right leads to an end linked up with the remaining part of the coupled chain (*i.e.*, $m - 1$ coupled primary chains).

If a monomer of the second primary chain is a root, then the left end is connected with the first primary chain and the right end is linked to the remaining part consisting of $m - 2$ primary chains. In the general case where a monomer of the jth primary chain furnishes the root, the left end is coupled with the chain fraction of $j - 1$ primary chains, and the right end is coupled with the remaining fraction of $m - j$ primary chains.

There is a one-to-one correspondence between the number of repeat units in the jth primary chain and the number of trees in the jth group, since each repeat unit of a primary chain has to be considered as a root. In the following we confine ourselves to homopolymers, *i.e.*, all primary chains are assumed to have the same degree of polymerization and the same composition.[28] The procedure of averaging consists now in averaging over all elements of a group followed by averaging over all groups.

3.2. Generating Function. As already pointed out, the two branches emerging from a root are not statistically equivalent. Therefore, a directional dependence of coupling has to be considered for each of the m groups of trees before the path weighting generating function can be set up. This directional dependence will be recognized from the tree graphs given in Figure 2b.

Now the path weighting generating function can be set up for each of the m groups. For the units in the zeroth generation the generating function of the two non-alike branches has to be multiplied; this yields

1st p. ch.[29] $U_{0(1)} = \theta^{\phi_0}(1 - \alpha + \alpha U_{1(1,0)})((1 - \alpha)U_{1(2,3)} + \alpha U_{1(1,2)})$

2nd p. ch. $U_{0(2)} = \theta^{\phi_0}((1 - \alpha)U_{1(1,0)} + \alpha U_{1(2,1)})((1 - \alpha)U_{1(3,4)} + \alpha U_{1(2,3)})$

jth p. ch. $U_{0(j)} = \theta^{\phi_0}((1 - \alpha)U_{1(j-1,j-2)} + \alpha U_{1(j,j-1)})((1 - \alpha)U_{1(j+1,j+2)} + \alpha U_{1(j,j+1)})$

mth p. ch. $U_{0(m)} = \theta^{\phi_0}((1 - \alpha)U_{1(m-1,m-2)} + \alpha U_{1(m,m-1)})(1 - \alpha + \alpha U_{1(m,0)})$ (23)

The generating function of the whole coupled chain is given by (see also footnote eq F24)

$$U_0 = \frac{1}{m}\sum_{j=1}^{m} U_{0(j)} \tag{24}$$

The expressions in the left parentheses represent the left branches of the tree in Figure 2b, while the right parentheses represent the right branches. The meaning of the indices will now be discussed for the example of the jth generating function.

The first subscript of a generating function always denotes the generation. The first index in the bracket indicates the primary chain to which the monomer units of consideration belong. The second index denotes the coupled primary chain to the left, if it is smaller than the first index, while it denotes the primary chain to the right, if it is larger than the first index.

$\alpha U_{1(j,j-1)}$ represents the probability of a linkage in the first generation between the root of the tree and a monomer of the chain $(j,\ j - 1)$ in the first generation. $(1 - \alpha)U_{1(j,j-1)}$ represents the probability of a linkage in the first generation between the root and a monomer of the neighbored primary chain $(j - 1,\ j - 2)$. A corresponding nomenclature applies to the linkages of the right branch. For the elements of the first, second, . . . nth generation only one branch sprouts instead of the two for an element in the zeroth generation. The generating functions of the nth generation ($n \geq 1$) are in analogy to eq 23.

Generating functions for the left branch

$$\begin{aligned}
U_{n(1,0)} &= \theta^{\phi_n}(1 - \alpha + \alpha U_{n+1(1,0)}) \\
U_{n(2,1)} &= \theta^{\phi_n}((1 - \alpha)U_{n+1(1,0)} + \alpha U_{n+1(2,1)}) \\
U_{n(j,j-1)} &= \theta^{\phi_n}((1 - \alpha)U_{n+1(j-1,j-2)} + \alpha U_{n+1(j,j-1)}) \\
U_{n(m,m-1)} &= \theta^{\phi_n}((1 - \alpha)U_{n+1(m-1,m-2)} + \alpha U_{n+1(m,m-1)})
\end{aligned} \tag{25a}$$

Generating functions for the right branch

$$\begin{aligned}
U_{n(1,2)} &= \theta^{\phi_n}((1 - \alpha)U_{n+1(2,3)} + \alpha U_{n+1(1,2)}) \\
U_{n(2,3)} &= \theta^{\phi_n}((1 - \alpha)U_{n+1(3,4)} + \alpha U_{n+1(2,3)}) \\
U_{n(j,j+1)} &= \theta^{\phi_n}((1 - \alpha)U_{n+1(j+1,j+2)} + \alpha U_{n+1(j,j+1)}) \\
U_{n(m,0)} &= \theta^{\phi_n}(1 - \alpha + \alpha U_{n+1(m,0)})
\end{aligned} \tag{25b}$$

Differentiation of U_0 with respect to θ at $\theta = 1$ yields a general expression for conformational averages (see Appendix II).

$$U_0'(1) = \phi_0 + \frac{2}{m}\sum_{j=1}^{m}(m - j + \alpha)(1 - \alpha)^{j-1} \times \left\{\sum_{i_1=1}^{\infty}\alpha^{i_1-1}\sum_{i_2=1}^{\infty}\alpha^{i_2-1}\ldots\sum_{i_j=1}^{\infty}\alpha^{i_j-1}\phi_{i_1+i_2+\ldots i_j}\right\} \tag{26}$$

Here i_j means the ith element of the jth primary chain, and $\phi i_1 + i_2 + \ldots i_j$ is the corresponding weighting function for distances of the path length $i_1 + i_2 + \ldots i_j$.

The j-fold sum in the curled brackets takes into account all possible distances between two chain elements of the coupled chain; thus it obeys the condition for the calculation of conformational averages given in eq 1. The frequency of the various distances is given by the coefficients α^{i_j-1}. The final sum performs the averaging over all the m groups of the trees.

Equation 26 reduces to the already-discussed case of a linear chain with a most probable distribution for the noncoupled chain ($m = 1$).

$$U_0'(1) = \phi_0 + 2\alpha\sum_{i_1=1}^{\infty}\alpha^{i_1-1}\phi_{i_1} \tag{6}$$

3.3. Special Averages. As was shown in section 1.2 the different averages are obtained by inserting special weighting functions.

Degree of Polymerization[30]

$\phi_n = 1$ $\qquad U_0' = DP_w$

Using eq 26 the degree of polymerization is found to be

$$DP_w = 1 + \frac{2}{m}\sum_{j=1}^{m}\frac{m - j + \alpha}{1 - \alpha} = \frac{m + \alpha}{1 - \alpha} \tag{27}$$

Mean-Square Radius of Gyration

$\phi_n = \langle r_n^2\rangle$ $\qquad U_0' = 2DP_w\langle S^2\rangle_z$

Here we have to distinguish between the two cases of very long and flexible chains (the region of Gaussian behavior) and of stiff chains.

For *Gaussian chains* the weighting function is

$$\phi_n = \langle r_n^2\rangle = b_{\text{eff}}^2 n$$

Thus, for coupled Gaussian chains the mean-square radius of gyration is obtained as

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[28] For block copolymers the path weight generating function is given by

$$U_0(\theta) = \sum_{j=1}^{m} C_j U_{0(j)}(\theta) \tag{F24}$$

Here C_j is the mass fraction of the jth primary chain of a special chemical composition, and U_{0j} is the corresponding generating function of the jth primary chain. If all primary chains have the same average length and the same chemical composition, we have $C_j = 1/m$ for all j's.

[29] p. ch. = primary chain.

[30] According to Schulz[5] the number-average degree of polymerization is

$$DP_n = mDP_{n(\text{p.ch.})} = m/(1 - \alpha) \tag{F27}$$

where $DP_{n(\text{p.ch.})}$ is the number-average degree of polymerization of a primary chain.

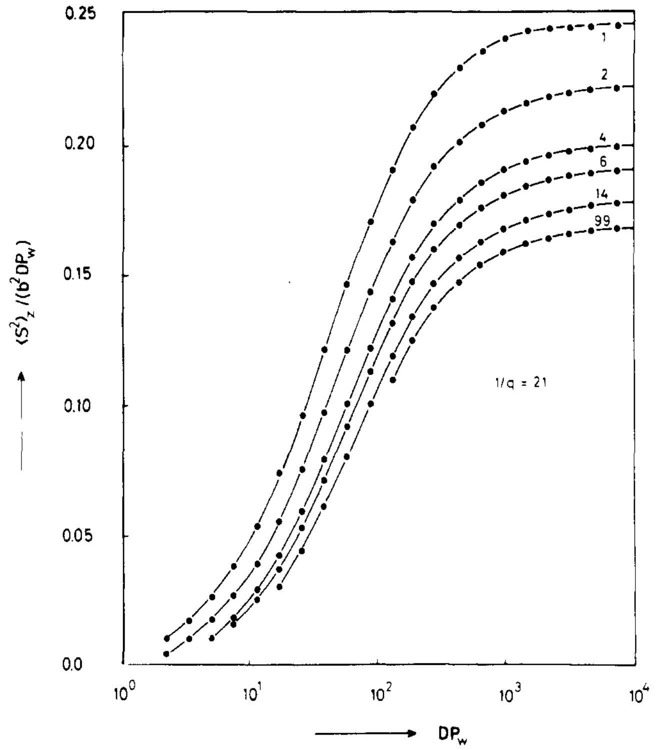

Figure 3. The z-average mean-square radius of gyration as function of the weight-average degree of polymerization for chains of a certain stiffness (21 monomer units/persistence length) and of various values of heterogeneity. The figures on the curves indicate the number of primary chains per molecule. (The heterogeneity is $M_w/M_n = 2$ for 1 primary chain and $M_w/M_n = 1.01$ for 99 primary chains.)

$$\langle S^2\rangle_z = b_{eff}{}^2\frac{\sum_{j=1}^{m} j(m - j + \alpha)}{m(1 - \alpha)(m + \alpha)} = \frac{b_{eff}{}^2}{6}\frac{m^2 - 1 + 6\alpha}{(1 - \alpha)(m + \alpha)} \tag{28}$$

For *stiff chains* the corresponding relationship for the weighting function is given by eq 16 when inserted into eq 26.

$$\langle S^2\rangle_z = \langle S^2\rangle_z{}^{\text{Gauss}} - b_{eff}{}^2\frac{1 - q}{q(2 - q)} \times \left(1 - \frac{1}{DP_w}\left[1 + \frac{2}{m(1 - \alpha)}\sum_{j=1}^{m}(m - j + \alpha) \times \left(\frac{(1 - \alpha)(1 - q)}{1 - \alpha(1 - q)}\right)^j\right]\right) \tag{29}$$

where $\langle S^2\rangle_z{}^{\text{Gauss}}$ is given by eq 28.

Particle Scattering Factor

$$\phi_n = \left\langle\frac{\sin hr_n}{hr_n}\right\rangle \qquad U_0' = DP_wP_z(\Theta)$$

Again, two different cases have to be distinguished for the Fourier transform: (a) for long *Gaussian chains* (see eq 10) the particle scattering factor is found to be

$$P_z(\Theta) = \frac{1}{DP_w}\left\{1 + \frac{2}{m}\sum_{j=1}^{m}\frac{m - j + \alpha}{1 - \alpha}\left[\frac{(1 - \alpha)Z}{1 - \alpha Z}\right]^j\right\} \tag{30}$$

(b) for *stiff chains*, on the other hand, the Fourier transforms of the spatial distance distributions are represented by eq 21. Thus, the particle scattering factor of stiff chains is obtained from eq 26.

$$P_z(\Theta) = \frac{1}{DP_w}\left\{(1 + C_1X^2) \times \left(1 + \frac{2}{m}\sum_{j=1}^{m}\frac{m - j + \alpha}{1 - \alpha}\left[\frac{(1 - \alpha)Z}{1 - \alpha Z}\right]^j\right) - \frac{1}{3}C_2X^4 \times \left(\frac{1}{m}\sum_{j=1}^{m}\frac{m - j + \alpha}{(1 - \alpha)(1 - \alpha Z)}j\left[\frac{(1 - \alpha)Z}{1 - \alpha Z}\right]^j\right)\right\} \tag{31}$$

Molecular Weight Distribution. Generating functions are also useful for the derivation of probability distribution functions. For instance, the weight distribution function for molecules built up of m coupled primary chains is derived from eq 24 and 25 as follows. Setting $\phi_n = 1$, one obtains for the weight generating function the analytic expression

$$W(\theta) = \theta^m\left[\frac{1 - \alpha}{1 - \alpha\theta}\right]^{m+1} \tag{32}$$

This equation may be written as a power series in terms of θ^x

$$W(\theta) = (1 - \alpha)^{m+1}\sum_0^\infty\frac{x!}{m!(x - m)!}\alpha^{x-m}\theta^x \tag{33}$$

As by definition

$$W(\theta) = \sum_0^\infty w(x)\theta^x$$

where $w(x)$ is the weight distribution function for chains of $DP = x$, one has

$$w(x) = \frac{x!}{m!(x - m)!}(1 - \alpha)^{m+1}\alpha^{x-m} \tag{34}$$

This distribution becomes for $x \gg m$

$$w(x) \longrightarrow \frac{x^m}{m!}(1 - \alpha)^{m+1}\alpha^x \tag{35}$$

which approaches the familiar Schulz-Zimm[5,6] distribution if $\alpha \cong 1$

$$w(x) \longrightarrow \frac{x^m}{m!}y^{m+1}\exp(-yx) \tag{36}$$

where $y = 1 - \alpha = m/DP_n$.

4. Computations and Discussion

The derived formulas for the linear chains with various heterogeneities are relatively simple and are, at least formally, valid for all degrees of polymerization. There is a clear correspondence between the number of coupled primary chains, m, and the heterogeneity M_w/M_n. The latter follows from the equations for the weight- and number-average molecular weights (see eq 27 and F27).

$$M_w/M_n = 1 + (\alpha/m) \tag{37}$$

This result is in agreement with the early findings of Schulz.[1] Thus with increasing number of coupled primary chains the polymer becomes more homogeneous.

Figure 3 shows the dependence of $\langle S^2\rangle_z$ on DP_w for a molecule with a persistence length of $a = b/q = 21b$. Since in all cases $\langle S^2\rangle_z$ decreases with increasing m values, we found it more instructive to use reduced $\langle S^2\rangle_z$ values

$$\frac{\langle S^2\rangle_z}{\langle S^2\rangle_{z\infty}} = \frac{\langle S^2\rangle_z}{DP_w}\bigg/\left(\frac{\langle S^2\rangle_z}{DP_w}\right)_\infty \tag{38}$$

where $\langle S^2\rangle_{z\infty}$ is the corresponding value to $\langle S^2\rangle_z$ at very large degrees of polymerization (Gaussian region).

Figure 4 demonstrates the DP dependence of the fol-

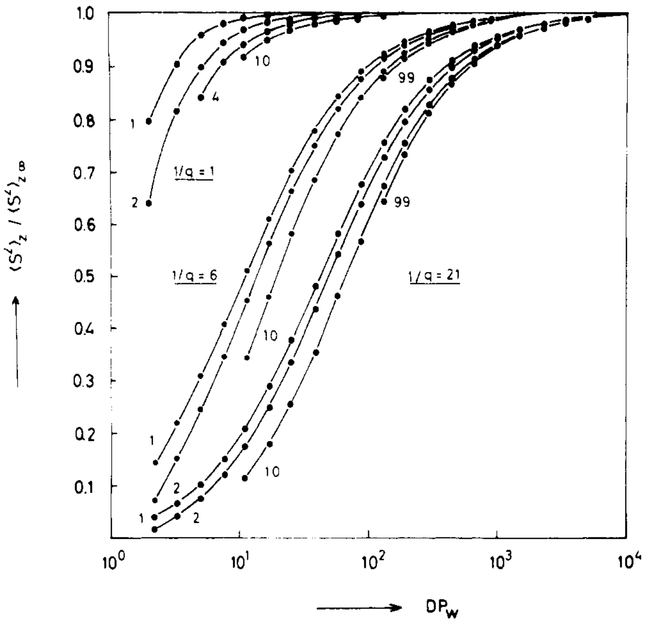

Figure 4. Dependence of the reduced-mean-square radius of gyration $\langle S^2\rangle_z/\langle S^2\rangle_{z\infty}$ on the degree of polymerization for chains of various heterogeneities and flexibilities. Meaning of the figures as in Figure 3; for the definition of the ordinate see eq 33.

lowing three cases: (i) a completely flexible chain, $1/q = 1$; (ii) a chain with a certain limited flexibility, $1/q = 6$; (iii) a stiff chain, $1/q = 21$. While case i has no physical counterpart, case ii is typical for synthetic polymers like poly(methyl methacrylate) and polystyrene, and case iii is found for cellulose derivates.

In all cases characteristic deviations from Gaussian behavior are observed at low DP_w. These deviations resemble the already known behavior of homodisperse stiff chains. Consider a point of deviation where $\langle S^2\rangle_z/\langle S^2\rangle_{z\infty}$ has reached a value of 0.75; this point migrates from very low DP_w values to higher ones with increasing chain stiffness. A similar, less pronounced shift is obtained with increasing m values, *i.e.*, with decreasing heterogeneity. Thus, the curves for polydisperse chains seem to indicate a lower chain stiffness than the chain in reality has.

The deviations from Gaussian behavior calculated for ideal, flexible chains, *i.e.*, $\cos\gamma = 0$, appear surprising at first sight. These deviations are caused, however, by the effect of the *finite* chain length, and the same holds also for stiff chains. The chain stiffness essentially reduces the number of statistically equivalent bonds, and to achieve Gaussian behavior, a sufficiently large number of statistically independent bonds are required.

The effect of chain stiffness and heterogeneity on the particle scattering factor is demonstrated in Figures 5 and 6. Here an increasingly marked downturn occurs with decreasing m values (increasing heterogeneity) and also with increasing chain stiffness. This reflects a well-known feature according to which it may be very difficult to decide whether an observed downturn is due to a high chain stiffness or due to a considerable heterogeneity. One notices, however, that for homodisperse chains the downturn at large angles is preceded by an upturn at small angles. This is not the case for polydisperse stiff chains. Therefore, accurate measurements at small as well as at large angles are necessary for a reliable interpretation of the scattering data.

Some Concluding Remarks. The analytic expressions derived in this paper appear to us to be of advantage for the following reasons. As is well known, Zimm plots of scattering data simultaneously provide information on the molecular weight M_w, the particle scattering factor $P_z(\Theta)$ and the mean-square radius of gyration $\langle S^2\rangle_z$. In cascade theory the same averages are obtainable as special cases of a general generating function. Thus, there is a one-to-one correspondence between physical and theoretical pictures.

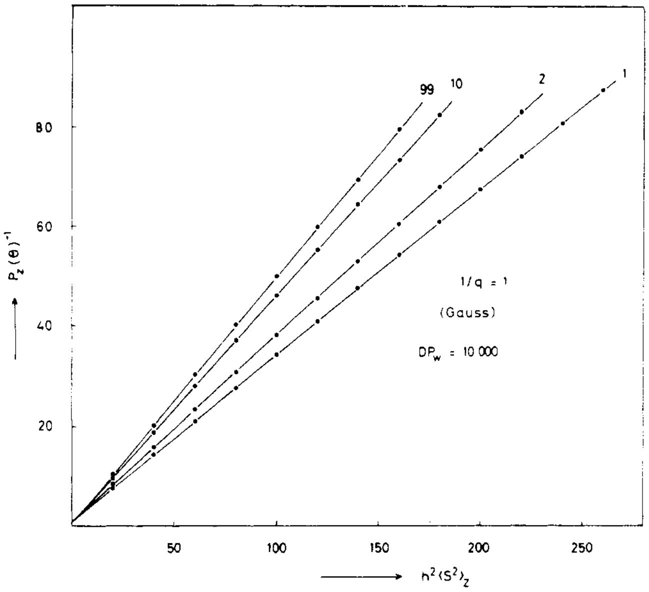

Figure 5. Influence of heterogeneity (chain coupling) on the z-average particle scattering factor of Gaussian chains. The number of primary chains is indicated by the figures on the curves.

Furthermore, a cascade process is a discrete process and cascade theory inherently takes account of the discrete nature of real chain molecules and of the corresponding molecular weight distribution. In some cases this fact is of importance for a more detailed description of chain conformations. For instance, the number of residues per turn, together with the persistence length, is an essential parameter of helically wound chains. Relationships derived previously for the mean-square distances $\langle r_n^2\rangle$ in a discrete homodisperse semiflexible helix[31] can directly be inserted in eq 26 when the influence of heterogeneity on the scattering behavior is of interest. A further advantage is given by the fact that the expressions derived by cascade theory are not restricted to long-chain molecules, but are, at least mathematically, valid for all degrees of polymerization.

Finally, from the mathematical point of view it seems worth mentioning that this treatment deals with a long-range correlation (after n generations) by distinguishing between the two functionalities on both sides of a repeat unit selected at random. With respect to a reacting monomer this difference is not evident, but it becomes clear on the consideration of tree structures (given in Figure 2b), which is the basis of the cascade theory.

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Appendix I

Weighting Function for the Particle Scattering Factor. The characteristic function $\phi(h,\psi)$ for the distance distribution of two chain elements is expressed by Daniels[19] as a series of Legendre polynomials

$$\phi(h,\psi) = \sum_{s=0}^{\infty}\phi_s(h)P_s(\cos\psi) \qquad \text{(A1)}$$

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(31) W. Burchard, *Brit. Polym. J.*, 3, 209, 214 (1971).

where ψ is an angle of orientation. The average of $\phi(h,\psi)$ taken over all orientations is the weighting function $\phi_n = \langle \sin hr_n/hr_n \rangle$ required for the calculation of particle scattering factors.[18] Daniels calculated the two first members of the series in eq A1 and found for the angular independent part[19]

$$\phi_n = \left\langle \frac{\sin\ hr_n}{hr_n} \right\rangle = \left\{1 + \frac{1}{3}\frac{g_1}{(1 - g_1)^2}h^2b^2 + \left[-\frac{1}{20}\frac{3 + 4g_1 + 3g_1^2}{1 - g_1^2} + \frac{1}{10}\frac{1 + g_2}{1 - g_2}\right] \times \frac{1}{q}\frac{(1 + g_1)^2}{(1 - g_1)^2}h^4b^4 \cdot n\right\} \exp\left(-\frac{1}{6}\frac{1 + g_1}{1 - g_1}h^2b^2n\right) \quad \text{(A2)}$$

For chains with fixed bond angles γ the coefficients g_1 and g_2 are Legendre polynomials of the bond angle

$$g_1 = \cos\ \gamma$$

$$g_2 = \frac{1}{2}(3\cos^2\ \gamma - 1) \quad \text{(A3)}$$

Introducting the persistence length a and a stiffness parameter q

$$a = b/(1 - \cos\ \gamma)$$

$$q = b/a = 1 - \cos\ \gamma$$

into eq A2 one arrives at

$$\left\langle \frac{\sin\ hr_n}{hr_n} \right\rangle = \left\{1 + \frac{1}{3}\frac{1 - q}{q^2}h^2b^2 + \left[-\frac{1}{20}\frac{3 + 4(1 - q) + 3(1 - q)^2}{1 - (1 - q)^2} + \frac{1}{10}\frac{1 + \frac{1}{2}(3(1 - q)^2 - 1)}{1 - \frac{1}{2}(3(1 - q)^2 - 1)}\right]\frac{1}{9}\frac{2 - q}{q^2}h^4b^4n\right\} \times \exp\left(-\frac{1}{6}\frac{2 - q}{q}h^2b^2n\right) \quad \text{(A4)}$$

This equation can be written in the alternative form

$$\left\langle \frac{\sin\ hr_n}{hr_n} \right\rangle = [1 + C_1X^2]Z^n + C_2X^4\frac{\mathrm{d}}{\mathrm{d}X^2}(Z^n) \quad \text{(A5)}$$

where the abbreviations were used

$$C_1 = \frac{1}{3}\frac{1 - q}{q(2 - q)}$$

$$C_2 = \frac{1}{30}\frac{(22/3) - 6q + q^2}{q(2 - q)} \quad \text{(A6)}$$

$$X^2 = h^2b^2[q/(2 - q)]$$

$$Z = \exp(-X^2/6)$$

Appendix II

Derivation of Eq 26. When differentiating eq 23 with respect of θ at $\theta = 1$, the following relationship is obtained

$$U_0'(1) = \frac{1}{m}\left\{m\phi_0 + (1 - \alpha)\sum_{j=2}^{m}U_{1(j-1,\,j-2)}' + \alpha\sum_{j=1}^{m}U_{1(j,\,j-1)}' + (1 - \alpha)\sum_{j=1}^{m=1}U_{1(j+1,\,j+2)}' + \alpha\sum_{j=1}^{m}U_{1(j,\,j+1)}'\right\}. \quad \text{(A7)}$$

where use was made of eq 24. The two first sums can be simplified

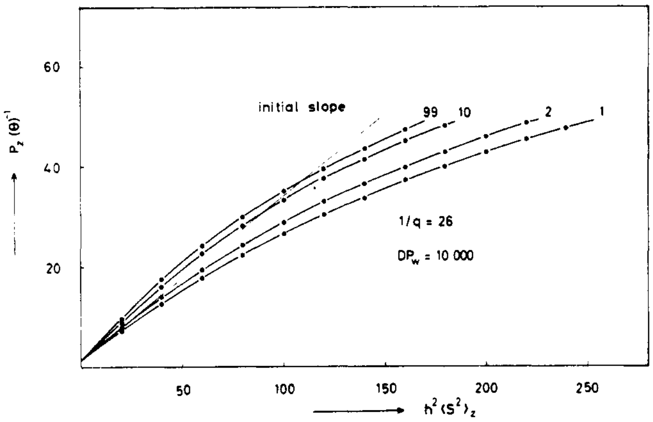

Figure 6. Influence of heterogeneity on the particle scattering factor of a moderately stiff chain. $1/q = 26$ is the number of monomer units per persistence length. Meaning of the other figures as in Figure 5.

$$(1 - \alpha)\sum_{j=2}^{m}U_{1(j-1,\,j-2)}' + \alpha\sum_{j=1}^{m}U_{1(j,\,j-1)}' = (1 - \alpha)\sum_{j=1}^{m-1}U_{1(j,\,j-1)}' + \alpha\sum_{j=1}^{m'}U_{1(j,\,j-1)}' = \sum_{j=1}^{m-1}U_{1(j,\,j-1)}' + \alpha U_{1(m,\,m-1)} \quad \text{(A8)}$$

and a similar simplification is possible for the two last sums in eq A7. Thus

$$U_0'(1) = \phi_0 + \frac{1}{m}\left[\sum_{j=1}^{m-1}(U_{1(j,\,j-1)}' + U_{1(j-1,\,j)}') + \alpha(U_{1(m,\,m-1)}' + U_{1(1,\,2)})\right] \quad \text{(A9)}$$

Iterative differentiation of eq 25a yields

$$U_{1(1,\,0)}' = \phi_1 + \alpha U_{2(1,\,0)}' = \phi_1 + \alpha\phi_2 + \alpha^2U_{3(1,\,0)}' = \sum_{n=1}^{\infty}\alpha^{n-1}\phi_n \quad \text{(A10)}$$

The same result is obtained from the last line in eq 25b

$$U_{1(m,\,m-1)}' = \sum_{n=1}^{\infty}\alpha^{n-1}\phi_n = U_{1(1,\,0)}' \quad \text{(A11)}$$

Similarly from the second line in eq 25a one finds

$$\begin{aligned} U_{1(2,\,1)}' &= \phi_1 + (1 - \alpha)U_{2(1,\,0)}' + \alpha U_{2(2,\,1)}' \\ &= \sum_{i_1=1}^{\infty}\alpha^{i_1-1}\phi_{i_1} + (1 - \alpha)\sum_{i_2=1}^{\infty}\alpha^{i_2-1}U_{i_2+1(1,\,2)}' \\ &= \sum_{i_1=1}^{\infty}\alpha^{i_1-1}\phi_{i_1} + (1 - \alpha)\sum_{i_2=1}^{\infty}\alpha^{i_2-1}\sum_{i_1=1}^{\infty}\alpha^{i_1+1}\phi_{i_1+i_2} \end{aligned} \quad \text{(A12)}$$

and from the second last line in eq 25b

$$U_{1(m-1,\,m)}' = U_{1(2,\,1)}' \quad \text{(A13)}$$

Proceeding in eq 25a and eq 25b line by line one finally arrives at

$$U_{1(j,\,j-1)}' = \sum_{k=1}^{j}(1 - \alpha)^{k-1}\sum_{i_1=1}^{\infty}\alpha^{i_1-1}\sum_{i_2=1}^{\infty}\alpha^{i_2-1}\ldots\sum_{i_j=1}^{\infty}\alpha^{i_j-1}\phi_{i_1+i_2\ldots i_j} \quad \text{(A14)}$$

$$U_{1(m-j+1,\,m-j)}' = U_{1(j,\,j-1)} \quad \text{(A15)}$$

Therefore

$$U_0'(1) = \phi_0 + \frac{2}{m}\left[\sum_{j=1}^{m-1}(U_{1(j,j-1)}' + \frac{2\alpha}{m}U_{1(m,m-1)}' \right. \quad \text{(A16)}$$

Inserting eq A14 and collecting terms with same number of sums this results in eq 26

$$U_0'(1) = \phi_0 + \frac{2}{m}\sum_{j=1}^{m}(m - j + \alpha) \times \sum_{i_1=1}^{\infty}\alpha^{i_1-1}\sum_{i_2=1}^{\infty}\alpha^{i_2-1}\ldots\sum_{i_j=1}^{\infty}\alpha^{i_j-1}\phi_{i_1+i_2+\ldots i_j} \quad (26)$$

Comparison of the Conformational Map for Poly(L-proline) with Conformational Maps for Polysarcosine and Poly(N-methyl-L-alanine)[1]

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ABSTRACT: The presence of the four minima in the conformational map reported by Mark and Goodman for poly(N-methyl-L-alanine) has been confirmed. The conformational map reported by Tanaka and Nakajima for polysarcosine, however, is found to be incorrect due to their failure to consider several crucial interatomic contacts. The conformational maps for both polysarcosine and poly(N-methyl-L-alanine) are found to be sensitive to the orientation selected for the methyl groups. If the geometry of these polypeptides is made similar to that of poly(L-proline), the computations at ϕ = 120° reveal two regions of low energy, separated by approximately 180° rotation about ψ. The relative energies of these two minima are extremely sensitive to the geometry selected for the polypeptide, as has previously been found to be the case for poly(L-proline).

A recent treatment[2] of the internal dipeptide unit in poly(L-proline) containing peptide bonds in the planar-trans conformation is in agreement with the characteristic ratio observed for this polypeptide[3] and allows for flexibility of the pyrrolidine ring, which has been demonstrated experimentally by proton[4] and ^{13}C[5] magnetic resonance studies. Energy minima are obtained near ϕ, ψ = 110°, 350° and ϕ, ψ = 120°, 130°.[2,6] The precise location and energy of the minimum near ϕ, ψ = 120°, 130° is sensitive to the geometry of the pyrrolidine ring.[2,7] The energy at this minimum may be as little as ~1 kcal/mol greater than the energy at ϕ, ψ = 110°, 350° if the pyrrolidine ring geometry is suitably chosen.[2]

Conformational maps reported for the internal dipeptide unit in polysarcosine[8] and poly(N-methyl-L-alanine),[9] computed with χ_N = 0°,[6] report a low energy for ϕ, ψ = 110°, 350°, but do not exhibit a region of low energy near ϕ, ψ = 120°, 130°. These results[8,9] might appear to be in conflict with the conformational maps for poly(L-proline),[2] since it is difficult to understand why a conformation should be available to poly(L-proline) but not to polysarcosine. Consequently the conformational maps for polysarcosine and poly(N-methyl-L-alanine) have been recomputed. The results previously reported for poly(N-methyl-L-alanine)[9] were confirmed, but it was not possible to reproduce the conformational map reported for polysarcosine.[8] In each case the conformational map is sensitive to the selection of the χ_N. If χ_N and χ_1 are assigned so that the orientation of the methyl groups is similar to that of C^β and C^δ in poly(L-proline), the computed energy *vs.* ψ for ϕ near 120° does exhibit minima close to the locations found in the internal dipeptide of poly(L-proline).[2]

Calculational Procedure

The atoms considered in the computation for poly(N-methyl-L-alanine) are shown in Figure 1. The bond lengths and bond angles for poly(N-methyl-L-alanine) were the same as those used by Mark and Goodman[9] except when specifically stated to the contrary. In the computation for polysarcosine the three C^β atoms and attached hydrogen atoms were replaced by three hydrogen atoms. The bond lengths and bond angles for polysarcosine were the same as those used by Tanaka and Nakajima.[8] The nonbonded interaction was evaluated for each pair of atoms in Figure 1 whose distance of separation depends upon $\chi_{1,i-1}$, $\chi_{1,i}$, $\chi_{1,i+1}$, $\chi_{N,i}$, $\chi_{N,i+1}$, ϕ_i, or ψ_i utilizing the same functions used in the previous work.[8,9] The total number of interatomic distances used in the evaluation of the nonbonded energy was 171 for polysarcosine and 383 for poly(N-methyl-L-alanine). The torsional potentials about ϕ_i and ψ_i were also the same as those used previously.[8,9] The torsional barrier about χ_N was assumed to be identical with that about ϕ_i. A barrier height of 3 kcal/mol was used for torsion about χ_1.[10] Minima occur at ±60 and 180° for torsion about χ_N and χ_1. The electrostatic interaction of the peptide groups was computed by the same procedure used by Tanaka and Nakajima,[8] which assigns partial charges to C′, O, N, and C^N and assumes a dielectric constant of 3.5. The dihedral angles ω_{i-1}, ω_i, and ϕ_{i+1} were held constant at 0°; ψ_{i-1} was also held constant at 0° except when specifically stated to the contrary.

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(1) Supported by Grant No. GB-36055 from the National Science Foundation.

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(6) The convention used is described in J. T. Edsall, P. J. Flory, J. C. Kendrew, A. M. Liquori, G. Nemethy, G. N. Ramachandran, and H. A. Scheraga, *Biopolymers*, **4**, 130 (1966); *J. Biol. Chem.*, **241**, 1004 (1966); *J. Mol. Biol.*, **15**, 339 (1966). In addition C_i^N will signify the carbon atom of the methyl group attached to the nitrogen atom of residue i and $\chi_{N,i}$ will refer to rotation about the N_i–C_i^N bond, which is zero when the C_{i-1}'–N_i and C_i^N–H bonds are eclipsed. The direction of rotation is identical for $\chi_{1,i}$ and $\chi_{N,i}$

(7) N. Gō and H. A. Scheraga, *Macromolecules*, **3**, 188 (1970).

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