Conformational Properties of Multiply Twisted Ring Systems and Daisy-Like Structures

W. Burchard,* E. Michel, and V. Trappe

Institute of Macromolecular Chemistry, University of Freiburg, D-79104 Freiburg, Germany

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ABSTRACT: Two multiple ring systems are considered and relationships are derived for the angular dependence of the scattered light ($P(q)$), the radius of gyration (R_g) and the hydrodynamic radius (R_h). The two models of consideration are (i) the multiply twisted ring system and (ii) the daisy-like ring structure. The derivations are made on the basis of the Wang−Uhlenbeck theorem on Gaussian distributions for the static properties and the Kirkwood−Riseman preaverage approximation for the hydrodynamics. The derived particle scattering factors show significant differences for the two different ring systems. To distinguish the multiply twisted ring system from a linear open chain, it is necessary to measure the scattering intensity over a large q range. The daisy-like structures resemble star-branched macromolecules but with numbers of subrings 4 to 5 times smaller than the arm numbers in a star. Differences between the shrinking factors and the ρ parameter of the various systems are noticeable and can be used to discern these systems.

Introduction

In the last years the conformational properties of macromolecular rings became a topic of interest for an increasing number of groups. This interest certainly arose from the discovery of cyclic DNA structures and the observation that not only single rings are formed but also multiply twisted ring structures.[1−4] More recently, this behavior was also observed with fungal and algae polysaccharides,[5−7] which indicates that ring formation and twisting is not a unique feature of DNA but has to be considered more generally as a possible structure for long chain molecules. Nowadays the preparation of synthetic cyclic macromolecules is possible; thus a systematic study of twisting properties appears to be feasible.

Another form of cyclic structures can be realized for chains where strongly associating groups are attached at both ends of the chain.[8−10] At very low concentration a simple ring formation can be expected. However, when passing to higher concentrations, a transition to micellar structures will occur for common surfactants, with the essential difference that now both chain ends are forming the core such that the middle section of the chains form loops. Figure 1 shows the daisy-like structure that can be expected. Of course, more complex aggregates will be formed in the concentrated regime since now the two ends of a chain can be positioned in two different micellar cores.[11−13]

Our special interest in daisy-like structures and twisted rings originates from the fact that these structures can be considered as the simplest elements in microgels which are prepared by exclusive intramolecular cross-linking of a single chain.[14−16] Experimental data are already available, but a basic theoretical treatment of these structures is still missing.

In this paper we will confine our considerations to the angular dependence of the scattered light ($P(q)$), the radius of gyration (R_g), and the hydrodynamic radius (R_h) for twisted and micellar ring systems with equal-sized rings. The general equations for these quantities are given by the well-known sums[17]

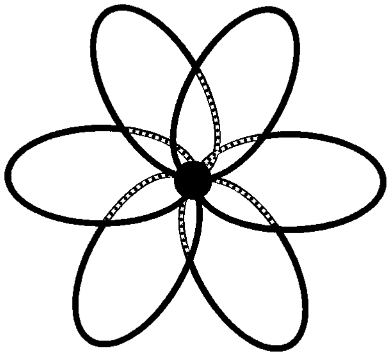

Figure 1. Example of a daisy-like or micellar ring system.

Particle scattering factor

$$P(q) = \frac{1}{N^2}\sum_s^N\sum_t^N\left\langle\frac{\sin qr_{st}}{qr_{st}}\right\rangle \tag{1}$$

Radius of gyration

$$R_g = \left(\frac{1}{2N^2}\sum_s^N\sum_t^N\langle r_{st}{}^2\rangle\right)^{1/2} \tag{2}$$

Hydrodynamic radius

$$R_h = \left(\frac{1}{N^2}\sum_s^N\sum_t^N\left\langle\frac{1}{r_{st}}\right\rangle\right)^{-1} \tag{3}$$

where $q = (4\pi n_o/\lambda_o)\sin(\theta/2)$, with n_o the refractive index of the solvent, λ_o the wavelength of the light used, and θ the scattering angle. N is the total number of segments for the considered macromolecule and r_{st} denotes the distance between the segments s and t. The equation of the hydrodynamic radius is based on the Kirkwood−Riseman preaveraging[17] of the Oseen tensor. This approximation is now generally accepted as being reasonably good for the description of the short-time diffusion behavior. As commonly known, R_h can be determined from the first cumulant of the time correlation function of the dynamic light scattering or from the sedimentation coefficient obtained by ultracentrifugation experiments.

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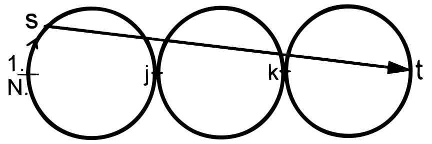

Figure 2. Example of a twisted ring. s and t denote two segments on two different rings.

The Wang–Uhlenbeck Formalism

We assume ideal flexibility such that the Gaussian statistic can be applied under the following constraints

- segment N is bound to the first segment (ring closure condition)
- on each twisting, two further segments are tethered together

We look for a general expression to describe the distance distribution between two segments s and t (see Figure 2). This problem was solved by Wang and Uhlenbeck[18] on the basis of multivariant Gaussian distributions. They found

$$W(r_{\mathrm{st}}) = \left(\frac{3}{2\pi b^2 |\mathbf{C}_m|/c^{mm}}\right)^{3/2} \exp\left\{-\frac{3}{2}\frac{c^{mm}}{|\mathbf{C}_m|}{r_{\mathrm{st}}}^2\right\} \quad (4)$$

which is again a Gaussian distribution with the variance that equals the mean square distance between the two segments of length b

$$\langle {r_{\mathrm{st}}}^2\rangle = b^2 \frac{|\mathbf{C}_m|}{c^{mm}} \quad (5)$$

With eq 4 for the distance distribution we find

$$\left\langle \frac{\sin qr_{st}}{qr_{st}} \right\rangle = \exp\left\{-\frac{b^2q^2}{6}\frac{|\mathbf{C}_m|}{c^{mm}}\right\} \quad (6)$$

and

$$\left\langle \frac{1}{r_{st}} \right\rangle = \left(\frac{6}{\pi b^2}\right)^{1/2} \left(\frac{c^{mm}}{|\mathbf{C}_m|}\right)^{1/2} \quad (7)$$

In these equations $\mathbf{C}_m$ denotes an $(m + 1) \times (m + 1)$ matrix where m is the number of subrings. $|\mathbf{C}_m|$ is the determinant of the matrix with c^{mm} the corresponding cofactor, i.e. the determinant of a matrix that is obtained by erasing the last row and column of the matrix $\mathbf{C}_m$. The elements c_{jk} ($j, k = 1, 2, ..., m$) of the $\mathbf{C}_m$ matrix can be easily found from a prescription that was deduced by Casassa[19] from the Wang–Uhlenbeck theorem

(1) The diagonal elements of the symmetric matrix contain the number of repeating units (r) of various subrings.

(2) The last element $c_{m+1,m+1}$ contains the number of units of the "ring" that is formed by the vector r_{st} and the chain section of the length $(t - s)$.

(3) The off-diagonal elements represent the number of repeating units that two different rings have in common.

In the following this prescription is applied to three examples (i) single Gaussian rings ($m = 1$), (ii) once twisted rings ($m = 2$), and (iii) m-membered twisted ring systems.

For the *single ring* we find

$$\mathbf{C}_1 = \begin{pmatrix} N & t-s \\ t-s & t-s \end{pmatrix} \quad (8)$$

and

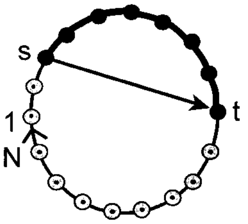

Figure 3. A single ring. The matrix elements of eq 8 can be found by inspection of this graph. See text.

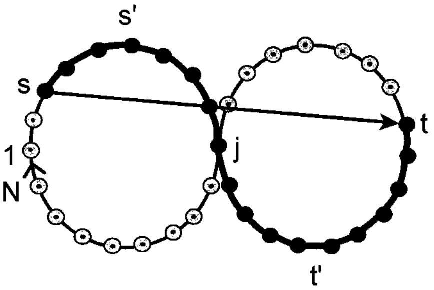

Figure 4. Two-membered once twisted ring. The matrix elements of eq 12 are found by inspection and the Casassa prescription. See text.

$$\frac{\mathbf{C}_1}{c^{11}} = N\frac{n}{N}\left(1 - \frac{n}{N}\right) \quad (9)$$

which inserted in eq 5 gives the well-known[19,20] result for the mean square distance of the segment pair (s,t)

$$\langle {r_{st}}^2\rangle = b^2 N(X(1 - X)) \quad (10)$$

with

$$X = (t - s)/N = n/N \quad (11)$$

For the *two membered ring syst*em with segments t and s on different subrings one finds

$$\mathbf{C}_2 = \begin{pmatrix} r_1 & 0 & s' \\ 0 & r_2 & t' \\ s' & t' & t-s \end{pmatrix} \quad (12)$$

with

$$s' = r_1/2 - s; \qquad t = t - r_1/2; \qquad (t - s) = t' + s'$$

and

$$\frac{|\mathbf{C}_2|}{c^{22}} = r_1\frac{s'}{r_1}\left[1 - \frac{s'}{r_1}\right] + r_2\frac{t'}{r_2}\left[1 - \frac{t'}{r_2}\right] \quad (13)$$

where $r_1 = r_2 = r$, i.e. equally sized rings are assumed.

Finally, for the *m-membered, twisted ring* we have

$$\mathbf{C}_m = \begin{pmatrix} r & 0 & 0 & .. & 0 & s' \\ 0 & r & 0 & .. & 0 & r/2 \\ 0 & 0 & r & .. & 0 & r/2 \\ .. & .. & .. & .. & .. & .. \\ 0 & 0 & 0 & .. & r & t' \\ s' & r/2 & r/2 & .. & t' & t'-s \end{pmatrix} \quad (14)$$

with

$$(t - s) = t' + s' + (m - 2)(r/2) \quad (15)$$

and

$$\frac{|\mathbf{C}_m|}{c^{mm}} = r\frac{s'}{r}\left[1 - \frac{s'}{r}\right] + r\frac{t'}{r}\left[1 - \frac{t'}{r}\right] + (m-2)\left(\frac{r}{4}\right) \tag{16a}$$

or

$$\frac{|\mathbf{C}_m|}{c^{mm}} = \frac{|\mathbf{C}_2|}{c^{22}} + (m-2)\left(\frac{r}{4}\right) \tag{16b}$$

We are ready now to derive the conformational parameters of eqs 1−3 which can be obtained by static and dynamic light scattering.

The Single Ring[19,20]

Inserting eq 9 into eq 6 and 1, one finds for the particle scattering factor

$$P_{1r}(q) = \frac{1}{N}\sum_{n=1}^{N}\exp\left[-\frac{q^2b^2}{6}N\left(\frac{n}{N} - \frac{n^2}{N^2}\right)\right] \tag{17a}$$

which for large N can be written as an integral

$$P_{1r}(q) = \int_0^N \exp\left[-\frac{q^2b^2}{6}NX(1-X)\right] \mathrm{d}X$$

where $X = (n/N)$ or

$$P_{1r}(q) = \left(\frac{2}{u_{1r}^{\;2}}\right)^{1/2} \boldsymbol{D}\left[\left(\frac{u_{1r}^{\;2}}{2}\right)^{1/2}\right] \tag{17b}$$

with $u_{1r}^2 = q^2R_{g,1r}^2$ and the Dawson integral $D(X) = \exp\{-X^2\}\int_0^x\exp\{t^2\}\,\mathrm{d}t$. The mean square radius of gyration of the ring is obtained by inserting eq 10 into eq 2

$$R_{g,1r} = \left(\frac{b^2N}{12}\right)^{1/2} \tag{18}$$

The sum of eq 3 for the hydrodynamic radius can be converted into an integral, which with eqs 7 and 9 eventually gives

$$R_{h,1r} = \left(\frac{b^2N}{6\pi}\right)^{1/2} \tag{19}$$

and

$$\rho_{1r} = \frac{R_{g,1r}}{R_{h,1r}} = \left(\frac{\pi}{2}\right)^{1/2} \tag{20}$$

The same results were obtained by Casassa[19] and Zimm and Stockmayer[20] who applied the convolution technique.

The Two-Membered Ring[21,22]

Equation 1 requires the summation over all pairs of segments. This can be done by first summing over those segment pairs which belong to the single rings (S_1) and then by summing the pairs with the two segments on different rings (S_{12}). Hence, we find for the two rings of equal size and $N = 2r$

$$P_{2r}(q) = \frac{1}{4}\left[\frac{2S_1}{r^2} + \frac{2S_{12}}{r^2}\right] = \frac{1}{2}[P_1(q) + P_{12}(q)] \tag{21}$$

The first term is evidently the particle scattering factor of a single ring ($P_{1r}(q)$) with its radius of gyration $R_{g,1r} = (rb^2/12)^{1/2}$. The second term is explicitly written as

$$P_{12}(q) = \left(\frac{1}{r}\sum_{s'}^{r}\exp\left\{-\frac{b^2rq^2}{6}X(1-X)\right\}\right) \times \left(\frac{1}{r}\sum_{t'}^{r}\exp\left\{-\frac{b^2rq^2}{6}Y(1-Y)\right\}\right)$$

with $X = s'/r$ and $Y = t'/r$. Comparison with eq 17 gives

$$P_{12}(q) = P_{1r}^{\;2}(q) \tag{22}$$

Therefore, the particle scattering factor of the two-membered ring is

$$P_{2r}(q) = \frac{1}{2}[P_{1r}(q) + P_{1r}2(q)] \tag{23}$$

Using the familiar expansion of the particle scattering factor

$$P(q) = 1 - \frac{1}{3}q^2R_g^{\;2} + ... \tag{24}$$

one finds

$$R_{g,2r} = \left[\frac{3}{2}R_{g1r}\right]^{1/2} = \left[\frac{b^2N}{16}\right]^{1/2} \tag{25}$$

The hydrodynamic radius has to be derived from eqs 7 and 3 which requires a somewhat tedious integration. The integrals were solved by Fukatsu and Kurata[21] and by Matuschek and Blumen[22] with the final result

$$R_{h,2r} = \left(\frac{b^2N}{6\pi}\right)^{1/2}\frac{2}{(2 - 2^{1/2})(2^{3/2} + 1)} \tag{26}$$

Combination of eqs 25 and 26 leads to the ρ parameter

$$\rho_{2r} = \frac{(6\pi)^{1/2}}{8}(2 - 2^{1/2})(2^{3/2} + 1) \tag{27}$$

The *m*-Membered Twisted Ring

We start again with the particle scattering factor. Here the sum over all segment pairs can be split as follows

$$P_{mr}(q) = \frac{1}{m^2r^2}\left[mS_1 + 2\sum_{j=1}^{m-1}(m-j)S_{1,j+1}\right] \tag{28}$$

where $mr = N$ and $S_{1,j+1}$ is given by

$$S_{1,j+1} = \sum_{s'}^{r}\sum_{t'}^{r}\exp\left\{-\frac{b^2q^2}{6}\frac{|C_{j+1}|}{c^{j+1,j+1}}\right\}$$

As shown in eq 22 for the case of S_{12} the double sum decomposes in a product of two single sums. The result is

$$S_{1,j+1} = r^2P_{1,j+1}(q) = r^2P_{1r}^{\;2}(q)\exp\left\{-\frac{q^2R_{g,1r}^{\;2}}{2}(j-1)\right\} \tag{29}$$

With eq 28 this yields

$$P_{mr}(q) = \frac{P_{1r}(q)}{m} + \frac{2}{m^2} P_{1r}{}^2(q) \sum_{j=1}^{m-1} (m-j) \exp\left\{-\frac{q^2 R_{g,1r}{}^2}{2}(j-1)\right\} \tag{30}$$

In the limit of $m \gg 1$ one finds after performing the summation of eq 30

$$P_{mr}(q) = \frac{P_{1r}(q)}{m} + P_{1r}{}^2(q)\frac{2}{a^4 m^2}[a^2 m - 1 + \exp(-a^2 m)] \tag{31}$$

with

$$a^2 = q^2 R_{g,1r}{}^2/2 \tag{32}$$

The second term in eq 31 represents the well-known Debye relationship[23] for the particle scattering factor of a Gaussian open chain if $P_{1r}(q) \rightarrow 1$.

The mean square radius of gyration $R_{g,mr}{}^2$ can be obtained directly from eq 30 by making use of eq 24. Alternatively, $R_{g,mr}{}^2$ is found by inserting eq 16b into eq 2 and performing the double summation over all segment pairs s' and t'. The result is

$$R_{g,mr} = \left(\frac{m+1}{2}\right)^{1/2} R_{g,1r} = \left(\frac{m+1}{2}\right)^{1/2}\left(\frac{b^2 N}{12m}\right)^{1/2} = \left(\frac{m+1}{4m}\right)^{1/2} R_{g,\mathrm{lin}} \tag{33}$$

which agrees with the result found by Yang and Yu[24] obtained by graph theory.[25,26] The derivation of the corresponding hydrodynamic radius is formed by inserting eq 16b into eq 7 which is a result of the Kirkwood–Riseman hydrodynamic preaverage approximation.[17] The summation over all segment pairs which are separated by $j - 2$ other subrings results in eq 34, derived previously by Fukatsu and Kurata[21]

$$R_{h,mr} = \left[1 + \frac{4}{m\pi}K\right]^{-1}\left(\frac{b^2 N}{6\pi}\right)^{1/2} = \left[1 + \frac{4}{m\pi}K\right]^{-1} m^{1/2} R_{h,1r} \tag{34}$$

where

$$K = \sum_{k}^{m-1} \sum_{j}^{m-k} [2 \arcsin(j^{-1/2}) - (j-1) \arcsin(j-1)] \tag{35}$$

The ρ parameter follows from eqs 33 and 34 and is

$$\rho_{mr} = \left(\frac{m+1}{2m}\right)^{1/2}\left(1 + \frac{4}{m\pi}K\right)\rho_{1r} \tag{36}$$

The Daisy-Like Ring System

All quantities can be easily derived from the results of the single ring and those from the two-membered ring system where the two segments s and t are positioned on two different subrings. Applied to the *particle scattering factor* this gives

$$P_{mr}(q) = \frac{1}{m}[P_{1r}(q) + (m-1)P_{12}(q)] = \frac{1}{m}[P_{1r}(q) + (m-1)P_{1r}{}^2(q)] \tag{37}$$

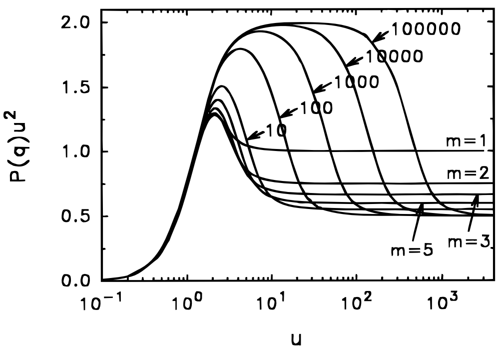

Figure 5. Kratky plots of the angular dependencies of multiply twisted ring systems. The figures on the curves denote the number of subrings in the system. A quasi linear behavior is obtained in the limit of many subrings. The decay at large $u = qR_g$ for the quasi linear structure arises from the particle scattering factor of the microstructure that in this case is a ring.

The corresponding mean square *radius of gyration* is derived from this equation under consideration of eq 24

$$R_{g,mr} = \left(\frac{2m-1}{m}\right)^{1/2} R_{g,1r} = \left(\frac{2m-1}{m}\right)^{1/2}\left(\frac{b^2 N}{12m}\right)^{1/2} = \left(\frac{2m-1}{2m^2}\right)^{1/2} R_{g,\mathrm{lin}} \tag{38}$$

The *hydrodynamic radius* has to be derived from eqs 7 and 13 inserted in eq 3. The evaluation of the double sum was made previously by Matuschek and Blumen[22] who found

$$R_{h,mr} = \frac{(2m)^{1/2}}{(2^{1/2}m + 1)(2^{1/2} - 1)}\left(\frac{b^2 N}{6\pi}\right)^{1/2} = \frac{(2m^2)^{1/2}}{(2^{1/2}m + 1)(2^{1/2} - 1)} R_{h,1r} \tag{39}$$

Combining eqs 38 and 39, one finds for the ρ parameter

$$\rho_{mr} = \left(\frac{2m-1}{2m}\right)^{1/2} \frac{(2^{1/2}m + 1)(2^{1/2} - 1)}{m}\rho_{1r} \tag{40}$$

Numerical Results and Discussion

In the following we compare the properties of the twisted ring system with those of the daisy-like structure. At this point we wish to emphasize that the applied Wang–Uhlenbeck formalism is quite general and includes the calculated results for the hydrodynamic radius derived by Fukatsu for the multiple twisted rings and by Blumen et al. for the daisy-like structures. All other results are derived here for the first time.

In addition the properties of the daisy-like structures are also compared with those of the star-branched molecules, since these two systems have several aspects in common.

Angular Dependence of the Scattered Light. Figure 5 shows the particle scattering factors of the twisted ring system in a normalized Kratky plot, where $u = qR_{g,mr}$. The behavior of a single ring is well-known.[19,27] The curve develops a maximum at $u \cong 2$ and an asymptotic plateau of $u^2P(u) \rightarrow 1$. With an increasing number of subrings two things happen.

(1) The height of the maximum increases and becomes significantly broader (note the logarithmic u scale). At very large numbers of subrings an intermediate plateau

is reached that has the same height as for the linear flexible chain ($u^2P(u) = 2$).

(2) However, even this curve decays to a lower asymptotic plateau, which for $m \gg 1$ approaches the value $u^2P(u) = {}^1/_2$. For a finite number of rings the asymptotic plateau value is

$$u^2P(u) = (m+1)/2m, \qquad \text{for } u \to \infty \tag{41}$$

The curve for large subring numbers is easily understood. The plateau in the intermediate scattering region suggests a similarity between multiply twisted ring systems and linear chains. This could have been anticipated, since for large enough m a multiply-twisted ring system looks like a chain with cyclic subunits. Consequently, the final decay at very large u values is a result of probing a length scale where the "chain" microstructure is detected, in the present case that of a single ring. Hence, a very wide scattering range has to be applied (e.g. by combination of light and neutron scattering) before a reliable decision can be made whether a multiply-twisted ring or simply an open chain is present.

The corresponding daisy-like structures show a completely different scattering behavior which much more resembles that of star-branched macromolecules. Parts a and b of Figure 6 show the results. Only for the single ring is a constant plateau approached. In all other cases the curve decays asymptotically like $1/u^2$.

The single ring is well-known to show behavior that is very similar to a five-arm star-branched macromolecule.[28] The two-membered ring system corresponds to an eight-arm star, the three-membered equals widely the ten-arm star, and for a large number of rings we have asymptotically similar behavior for

$$f = 4m, \qquad f \gg 1;\ m \gg 1 \tag{42}$$

This difference may be a surprise at first sight but is the consequence of a strong decrease in the entropy of the ring structures. While the arms of star molecules are fixed at one end, in a ring structure both ends of the chain are tethered together, and this causes a drastic reduction of the number of possible conformations.

Global Structure Parameters. A complete analysis of the scattering behavior is certainly important, but most laboratories have not the equipment to perform both LS and SANS measurements. Therefore, it is of interest to decide whether consistent conclusions can also be drawn from the radius of gyration and the hydrodynamic radius, which can be determined by static and dynamic light scattering measurements.

The ρ parameter proved to be a useful quantity for distinguishing structures.[29] For convenience of a better comparison the main relationships for the twisted and the micellar ring systems are repeated here.

Twisted ring system (superscript T)

$$\rho_{mr}^{T} = \rho_{1r}\left(\frac{m+1}{2m}\right)^{1/2}\left(1 + \frac{4}{m\pi}K\right) \tag{36}$$

with K as given by eq 35.

Micellar ring system (superscript D)

$$\rho_{mr}^{D} = \rho_{1r}\left(\frac{2m-1}{2m}\right)^{1/2}\frac{(2^{1/2}m+1)(2^{1/2}-1)}{m} \tag{40}$$

where the ρ parameter of the single flexible ring is given by eq 20.

Star molecules with f arms[30]

$$\rho_f^{\text{star}} = \frac{8}{3}\left(\frac{3f-2}{f\pi}\right)^{1/2}\frac{(f+2^{1/2})(2^{1/2}-1)}{f} \tag{43}$$

The dependence of the ρ parameter on m and f is shown in Figure 7. A strongly opposite behavior is obtained for the twisted and daisy-like ring systems. The ρ parameter of the twisted rings approach as expected the value 1.50 for open linear chains, whereas the daisy ring system decays to a much smaller value of 1.04. The asymptotic limit for the star molecules is 1.08, which may be just outside of the experimental error in good light scattering experiments but for arm numbers $f < 10$ the difference is clearly outside the experimental error. In conclusion we can state that in spite of being only a single parameter the ρ value is a useful quantity to estimate different polymer architectures.

If not both static *and* dynamic LS can be carried out, one can make use of the shrinking factors $g_x = R_{x,\text{ring}}/R_{x,\text{lin}}$ in which the corresponding radii of the ring system and the open chain are compared at the same molar mass or the same degree of polymerization. In particular for x = g and x = h we find for the three systems

Twisted ring system

$$g_g = \left(\frac{m+1}{4m}\right)^{1/2} \tag{44}$$

$$g_h = \frac{8}{3\pi}\left(1 + \frac{4}{m\pi}K\right) \tag{45}$$

Micellar ring systems (daisy)

$$g_g = \left(\frac{2m-1}{2m^2}\right)^{1/2} \tag{46}$$

$$gh = \frac{8}{3\pi}\frac{(2m)^{1/2}}{(2^{1/2}m+1)(2^{1/2}-1)} \tag{47}$$

Star-molecules[3]

$$g_g = \left(\frac{3f-2}{f^2}\right)^{1/2} \tag{48}$$

$$g_h = \frac{f^{1/2}}{(f+2^{1/2})(2^{1/2}-1)} \tag{49}$$

The curves for the two ring systems are shown in Figure 8a. Interestingly, in the limit of large ring numbers the g_g and g_h factors of the twisted system approach ${}^1/_2$ and not the limiting value 1.0 for the linear chain. The comparison between the daisy and the star-branched structure is given in Figure 8b. A good differentiation between these structures is possible that is especially pronounced for the two ring systems. However, highly accurate calibration curves for R_g and R_h as a function of M are needed for distinguishing the daisy ring system from f-arm star molecules.

The present two systems are evidently the simplest cases of complex ring systems. In further studies the condition of equally sized rings and symmetrical twisting have to be given up to find a more realistic

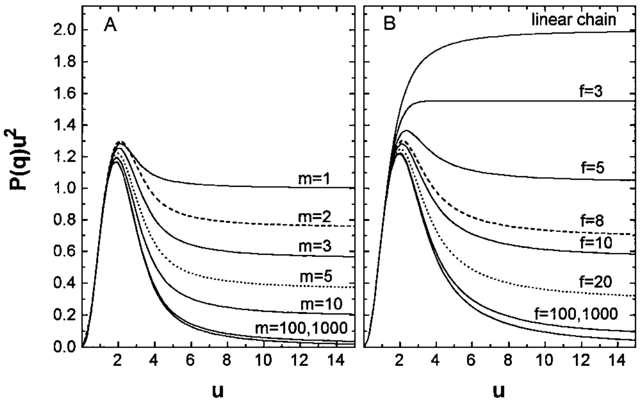

Figure 6. Kratky plots for the angular dependencies of daisy-like or micellar ring systems (a) in comparison to those of *f*-arm star molecules (b). The two topologies produce similar scattering behavior but with a number of arms in the star molecules that is 4−5 times larger than the ring numbers.

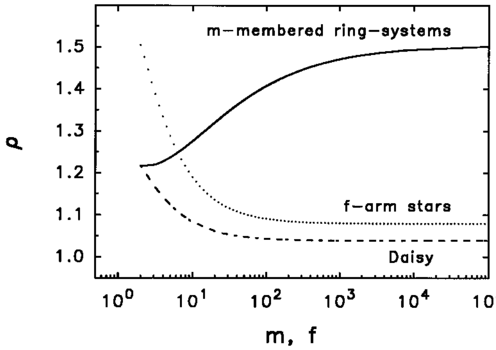

Figure 7. Comparison of the $\rho_x = R_{gx}/R_{hx}$ of the two ring systems and the *f*-arm star macromolecules. (x: twisted ring, daisy structure, star macromolecules).

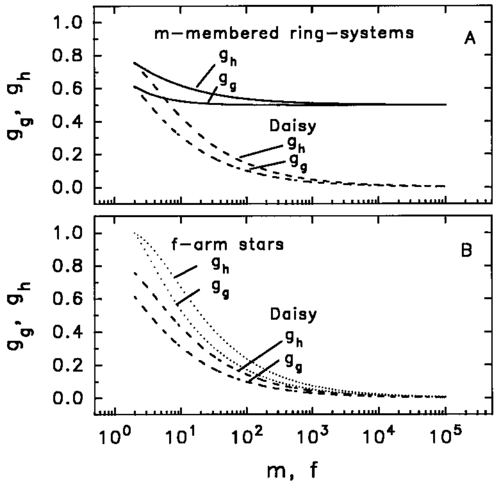

Figure 8. Comparison of the shrinking factors g_g and g_h for the three structures mentioned in Figure 7.

description of actually observed structures. On each twisting step a momentum of chain stiffening is introduced and this should eventually result in stiff double helices rather than in flexible ones as described in this paper. Finally, the effects of polydispersity and excluded volume has to be included. The second virial coefficient A_2 and the intrinsic viscosity $[\eta]$ are expected to exhibit even stronger structure dependence than the parameters based on radii. While the above mentioned structural modifications, polydispersity, and excluded volume effects probably can be successfully incorporated in the present theory,[31,33] we see at the moment no way to proceed with A_2 and $[\eta]$. For the former a renormalization group treatment may give a useful result,[28,32] but for the derivation of $[\eta]$ the relaxation spectrum has to be known.

In spite of the mentioned limitation of the idealized structures, we nonetheless think the present calculations demonstrate a first step toward a quantitative description of microgel structures.

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