Static and dynamic structure factors calculated for flexible ring macromolecules

Walther Burchard and Manfred Schmidt
Institute of Macromolecular Chemistry, University of Freiburg, West Germany
(Received 5 December 1979; revised 26 January 1980)

The influence of hydrodynamic pre-averaging on the first cumulant Γ of the dynamic structure factor of Gaussian ring molecules has been calculated. Similar to star-branched macromolecules, the relative error $\Delta\Gamma/\Gamma$ introduced by the pre-average approximation exhibits a maximum at intermediate $q = (4\pi/\lambda)\sin\theta/2$ which does not occur for the corresponding linear chain. This maximum is related to the increase of segment density by ring formation. The static structure factor also shows a maximum in the Kratky plot ($q^2\langle S^2\rangle P(q)$ against q^2) and has an asymptote at large q which is half that of linear chains. Furthermore, the $S{:}R$ ratio ($\langle S^2\rangle^{1/2}\langle R_h^{-1}\rangle$), which can be determined from combined integrated and quasi-elastic scattering, proves to be significantly lower than for the linear chain. Thus, ring molecules and open chains can easily be distinguished from combined integrated and quasi-elastic light scattering, without comparison with linear chains as has been necessary hitherto. The accuracy will be particularly high with instruments which allow the recording of both types of scattering measurements simultaneously.

INTRODUCTION

Akcasu and Gurol[1] have derived a general equation for the first cumulant of the time correlation function $g_1(t) = S(q,t)/S(q,0)$ which can be obtained from quasi-elastic scattering experiments, where $S(q,t)$ and $S(q,0)$ are the dynamic and static structure factors. Under common conditions, i.e. dilute solutions, $g_1(t)$ is related to the light scattering intensity correlation function $\langle i(0)i(t)\rangle$, which is actually measured, through:

$$\langle i(0)i(t)\rangle = A + B|g_1(t)|^2 \qquad (1)$$

where A and B are constants and where $g_1(t)$ is now the normalized electric field correlation function:

$$g_1(t) = \langle E(0)E^*(t)\rangle / \langle E(0)E^*(0)\rangle \qquad (2)$$

For monodisperse samples with small dimensions in comparison to the wavelength of the light, $g_1(t)$ decays exponentially:

$$g_1(t) = e^{-\Gamma t} = e^{-Dq^2t} \qquad (3)$$

where D is the translational diffusion coefficient of the Brownian particle and $q = (4\pi/\lambda)\sin\theta/2$, the value of the scattering vector.

For larger particles of geometrical anisotropy or for large chain molecules with internal mobility, the electric field correlation function shows considerable deviations from a single exponential. Still, the initial part can be approximated by a single exponential where, however, $\Gamma/q^2 = D_{\mathrm{app}}(q)$ is now a function of q.

The Akcasu–Gurol formula has the form:

$$\Gamma = \left.\frac{\mathrm{d}\ln g_1(t)}{\mathrm{d}t}\right|_{t=0} = \frac{\sum_j^N \sum_k^N \langle(\mathbf{q}\cdot\underline{\underline{\mathbf{D}}}_{jk}\cdot\mathbf{q})e^{i\mathbf{q}\mathbf{R}_{jk}}\rangle_{\mathrm{eq}}}{\sum_j^N \sum_k^N \langle e^{i\mathbf{q}\mathbf{R}_{jk}}\rangle_{\mathrm{eq}}} \equiv q^2\frac{\sum_j^N \sum_k^N \phi_{jk}^Q}{\sum_j^N \sum_k^N \phi_{jk}^I} \qquad (4)$$

where $\mathbf{R}_{jk} = \mathbf{r}_j - \mathbf{r}_k$, and the diffusion tensor is given by:

$$\underline{\underline{\mathbf{D}}}_{jk} = k_BT\left[\frac{\delta_{jk}}{\zeta}\mathbf{1} + \frac{1-\delta_{jk}}{8\pi\eta_0 R_{jk}}\left(\mathbf{1} + \frac{\mathbf{R}_{jk}\mathbf{R}_{jk}}{\mathbf{R}_{jk}^2}\right)\right] \qquad (5)$$

Equation (4) is noteworthy since only the *equilibrium* pair distance distribution, indicated in equation (4) by the subscript eq, is needed and not the full space-time distribution for the calculation of the measurable average. In many cases, and in particular for macromolecules in the unperturbed state, this equilibrium distribution is well known. Thus, it is possible to derive equations for the first cumulant of monodisperse and polydisperse linear chains[1–3], of regular and polydisperse star-macromolecules[3], of randomly

0032–3861/80/070745–05$02.00

and non-randomly branched polycondensates and of randomly cross-linked chains[4,5]. In all these cases the pair distance distribution is Gaussian:

$$W(\mathbf{R}_{jk})\mathrm{d}\mathbf{R}_{jk} = \left(\frac{3}{2\pi b^2|j-k|}\right)^{3/2} \exp\left[-\frac{3}{2}\frac{\mathbf{R}_{jk}^2}{b^2|j-k|}\right]\mathrm{d}\mathbf{R}_{jk} \tag{6}$$

The length distribution of a pair of elements in a ring-molecule differs from equation (6) by the constraint that the first and last chain elements of an open chain are linked together. According to this constraint, the pair distance distribution of ring elements is the convolution of the two Gaussian distributions $W(\mathbf{R}_{jk})$ and $W(\mathbf{R}_{Njk})$, where the subscript jk denotes a chain of $j-k$ elements while Njk denotes the complementary subchain, in the ring, of $N-|j-k|$ elements. Convolution of these two Gaussian distributions leads to the ring pair distance distribution[6]:

$$W_r(\mathbf{R}_{jk})\mathrm{d}\mathbf{R}_{jk} = \mathcal{N}\exp\left[-\frac{3}{2}\frac{\mathbf{R}_{jk}^2}{b^2}\left(\frac{1}{|j-k|}\,\frac{1}{N-|j-k|}\right)\right]\mathrm{d}\mathbf{R}_{jk} \tag{7a}$$

or

$$W_r(\mathbf{R}_{jk})\mathrm{d}\mathbf{R}_{jk} = \left(\frac{3}{2\pi b^2 N(1-n/N)(n/N)}\right)^{3/2} \exp\left[-\frac{3}{2}\frac{\mathbf{R}_{jk}^2}{b^2N(1-n/N)(n/N)}\right]\mathrm{d}\mathbf{R}_{jk} \tag{7b}$$

where for abbreviation $n = |j-k|$ is used.

The first cumulant

The average for the integrated scattering function from one pair of elements ϕ_{jk}^I is readily performed with the result[6,7]:

$$\phi_n^I = e^{-\nu^2[(1-n/N)(n/N)]} \tag{8}$$

where $n = |j-k|$ and

$$\nu^2 = b^2Nq^2/6 \tag{9}$$

The calculation of the corresponding pair function of the quasi-elastic scattering ϕ_{jk}^Q is more involved. Comparison of the equations for the ring molecule with those for the open chain reveals[3], however, that the final result is obtained from the relationships for the open chain by replacing the length of the open chain n by $N(1-n/N)(n/N)$. Hence:

$$\phi_n^Q = \frac{k_BT}{\zeta}\delta_n + (1-\delta_n)\frac{A}{[(1-n/N)(n/N)]^{1/2}}\,\frac{3}{4}\,[-x^2 + (2x^{-1}+x^{-3})D(x)] \tag{10}$$

with:

$$A = k_BT/(\eta_0 6^{1/2}\pi^{3/2}bN^{1/2}) \tag{11}$$

$$x^2 = \nu^2[(1-n/N)(n/N)] \tag{12}$$

and the Dawson integral:

$$D(x) = e^{-x^2}\int_0^k e^{t^2}\,\mathrm{d}t \tag{13}$$

Although the Dawson integral is tabulated[8], it offers some difficulties in subsequent handling when numerical data are required. Therefore, it appears desirable to use a satisfactory approximation for ϕ_n^Q. The following approximation was found to be accurate within 1% up to a value of $x^2 = 5$; beyond this argument, the approximated pair function decays more strongly but the function itself has decayed there already below 1/10 of its initial value[3]:

$$\phi_n^Q = \phi_{n,\mathrm{pre}}^Q + \Delta\phi_n^Q \tag{14}$$

where:

$$\phi_{n,\mathrm{pre}}^Q = \frac{k_BT}{\zeta}\delta_n + (1-\delta_n)\frac{A}{[(1-n/N)(n/N)]^{1/2}}\,e^{-\nu^2[(1-n/N)(n/N)]} \tag{15}$$

$$\Delta\phi_n^Q = 0.200A\nu^2[(1-n/N)(n/N)]^{1/2}\,e^{-a^2\nu^2[(1-n/N)(n/N)]} \tag{16}$$

with:

$$a^2 = 0.72 \tag{17}$$

The function $\phi_{n,\mathrm{pre}}^Q$ is the corresponding pair contribution to the quasi-elastic scattering when the hydrodynamic pre-average approximation is applied, i.e. if instead of the correct average of equation (4) the product of two averages $\langle\mathbf{q}\cdot\underline{\mathbf{D}}_{jk}\cdot\mathbf{q}\rangle\langle e^{i\mathbf{q}\mathbf{R}_{jk}}\rangle = \phi_{n,\mathrm{pre}}^Q$ is used.

Inserting equation (8) and equation (14)–(16) into equation (4) and passing to integrals, one obtains:

$$\Gamma = P(q)^{-1}\left\{k_BT/(\zeta N) + 2A\left[\int_0^{1/2}\frac{e^{-\nu^2(1-\xi)\xi}}{[(1-\xi)\xi]^{1/2}}\,\mathrm{d}\xi + 0.200\nu^2\int_0^{1/2}[(1-\xi)\xi]^{1/2}e^{-a^2\nu^2(1-\xi)\xi}\,\mathrm{d}\xi\right]\right\} \tag{18}$$

with the particle scattering function:

$$P(q) = S(q,0)/N^2 = 2\int_0^{1/2} e^{-\nu^2(1-\xi)\xi}\,\mathrm{d}\xi \tag{19}$$

The integrals can be brought into another form by the change of variables:

$$\xi = (1+t)/2 \tag{20}$$

which is useful for the integral in equation (19) for the particle scattering factor but not advisible for the integrals in equation (18). For the particle scattering factor one finds with equation (20):

$$P(q) = (2/\nu)e^{-\nu^2/4}\int_0^1 e^{(\nu^2/4)t^2}\,\mathrm{d}t = (2/\nu)D(\nu/2) \tag{21}$$

where $D(x)$ is the Dawson integral which is tabulated in ref 8. The parameter ν^2 is related to the mean-square radius of gyration of the ring by:

$$\nu^2 = b^2Nq^2/6 = 2\langle S^2\rangle q^2 = 2u^2 \tag{22}$$

Equation (18) is identical to the relationship derived by Casassa many years ago[7].

Recently Akcasu *et al.*[9] have given a review of the various techniques for the derivation of time correlation functions for the quasi-elastic scattering and the corresponding first cumulant. For the first cumulant of the Gaussian ring molecule they obtained an equation which is identical with the first two terms of our equation (18), as expected, since these authors applied the pre-average approximation.

COMPUTATIONS AND RESULTS

Behaviour at large and small q*-values*

The integrals in equations (18) and (19) cannot be solved in terms of elementary functions and have to be evaluated numerically. Some features of the first cumulant can be recognized, however, by considering the asymptotic behaviour at large q-values and in the limit of small q.

We first show that, as expected[3], the asymptote of Γ for rings becomes identical to that of the open linear chain. Inspection of the three types of integrals in equation (18) and (19) reveals that the integrands rapidly go to zero when ν^2 becomes large, such that a negligible value of the integrand is reached at values of x much smaller than 1/2. Hence, the quadratic term in $\nu^2(1-x)x$ can be safely neglected for large ν^2. The evaluation for Γ simplifies then to:

$$\Gamma \rightarrow q^2\frac{k_BT}{\zeta}\Bigg/\Bigg(2\int_0^{1/2}\nu^{-\nu^2x}\,\mathrm{d}x$$

$$+\,q^2A\,\frac{\displaystyle\int_0^{1/2}x^{-1/2}e^{-\nu^2x}\,\mathrm{d}x + 0.200\nu^2\int_0^{1/2}x^{1/2}e^{-a^2\nu^2x}\,\mathrm{d}x}{\displaystyle\int_0^{1/2}e^{-\nu^2x}\,\mathrm{d}x} \tag{23}$$

All integrals are well known and the evaluation yields:

$$\Gamma \rightarrow q^2\frac{k_BT}{\zeta N}\frac{\nu^2}{2}(1-e^{-\nu^2/2})^{-1}$$

$$+\,q^2A\pi^{1/2}\nu\left[\frac{\mathrm{erf}(\sqrt{\nu^2/2})}{1-e^{-\nu^2/2}} + 0.100/a^3\right.$$

$$\left.\frac{\mathrm{erf}(\sqrt{a^2\nu^2/2}) - 2\pi^{-1/2}e^{-a^2\nu^2/2}}{1-e^{-\nu^2/2}}\right] \tag{24}$$

Inserting equation (8) for ν^2 and taking into account that $\mathrm{erf}(\infty) = 1$, we find with $a^2 = 0.72$:

$$\Gamma \rightarrow \frac{b^2}{12}\frac{k_BT}{\zeta}q^4 + \frac{k_BT}{\eta_0}\frac{q^3}{6\pi}(1+0.100a^{-3})$$

$$= \frac{b^2}{12}\frac{k_BT}{\zeta}q^4 + 0.0617\frac{k_BT}{\eta_0}q^3 \tag{25}$$

which is indeed the asymptote of the open chain[3].

The behaviour of Γ in the limit of small q^2 is obtained by expanding the integrals into a power series:

$$\Gamma \xrightarrow[q^2]{\text{small}} q^2\frac{k_BT}{\zeta N}\left[2\int_0^{1/2}(1-\nu^2(1-x)x)\,\mathrm{d}x\right]^{-1}$$

$$+\,q^2A\,\frac{\displaystyle 2\int_0^{1/2}[(1-x)x]^{-1/2}\mathrm{d}x - (4/5)\nu^2/2\int_0^{1/2}[(1-x)x]^{1/2}\mathrm{d}x}{\displaystyle 2\int_0^{1/2}(1-\nu^2(1-x)x)\,\mathrm{d}x} \tag{26}$$

Integration yields:

$$\Gamma \xrightarrow[q^2]{\text{small}} q^2\left[\frac{k_BT}{\zeta N(1-\nu^2/6)} + A\,\frac{\pi-(\pi/10)\nu^2}{1-\nu^2/6}\right]$$

$$= q^2\left[\frac{k_BT}{\zeta N}(1+u^2/3) + A\pi(1+(2/15)u^2)\right] \tag{27}$$

where we have made use of equation (22). Since, in general:

$$\lim_{q\to 0}(\Gamma q^{-2}) = D \tag{28}$$

we find for the translational diffusion constant:

$$D = \frac{k_BT}{\zeta N} + \pi\frac{k_BT}{6^{1/2}\pi^{3/2}\eta_0 bN^{1/2}} \tag{29}$$

a result long known[10–13].

Numerical calculations

For the investigation of Γ in the intermediate q-region the integrals of equations (18) and (19) have to be solved

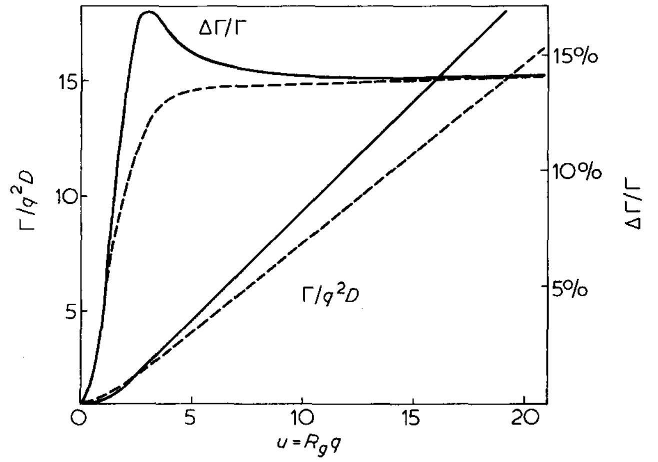

Figure 1 Angular dependence of the non-preaveraged and normalized first cumulant Γ/q^2D for flexible ring (———) and open chain (— — — —) macromolecules, and the relative error $\Delta\Gamma/\Gamma$ introduced by hydrodynamic pre-averaging. $\Delta\Gamma = \Gamma - \Gamma_{\rm pre}$, $R_g = \langle S^2\rangle^{1/2}$

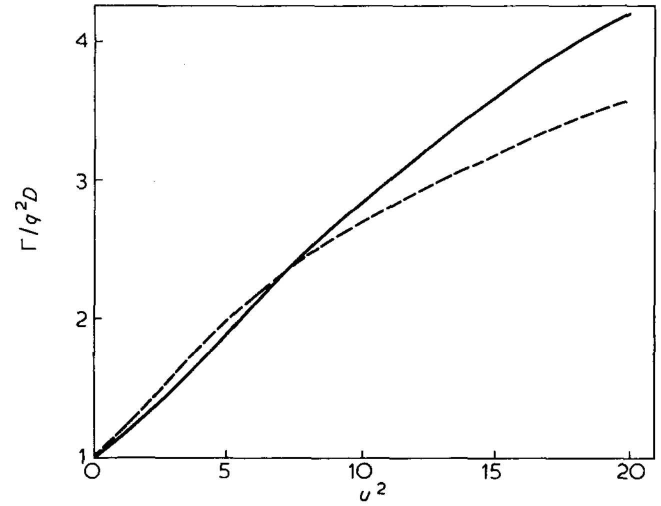

Figure 2 Normalized first cumulant Γ/q^2D as a function of $u^2 = q^2\langle S^2\rangle$ for ring (———) and chain (— — — —) molecules

numerically. The integration involves no difficulties with the exception of the first integral in equation (18) which at $\xi = 0$ has a singularity. However, the integral can be solved analytically for sufficiently small ξ-arguments; thus, we solved the integral by analytic integration for $\xi = 0$ to $\xi = 10^{-3}/\nu^2$ followed by numerical integration up to $\xi = 1/2$. The result is plotted in *Figures 1–4* in various ways, where we have neglected the free draining or Rouse term; or otherwise an assumption on the magnitude of the friction coefficient has to be made. The neglect of the Rouse term means restriction to large degrees of polymerization, an assumption implicitly contained already in the substitution of the double sum in equation (4) by integrals.

Figure 1 shows the angular dependence of the first cumulant as a function of $u = q\langle S^2\rangle^{1/2}$ in comparison to the behaviour of the open chain. At very low u-values, the angular dependence is slightly weaker for the ring-molecule than for the open chain, but the upturn at u-values around 2–3 is much stronger for the ring. At large u a straight line is obtained asymptotically with a slope of $d(\Gamma/q^2D)/du \rightarrow 0.9285$ which is a factor 1.2 larger than that of the open chain with $d(\Gamma/q^2D)/du \rightarrow 0.7735$.

Figure 2 shows the dependence of Γ/q^2D on u^2. The initial part in the power expansion in terms of u^2 has a slope of 2/15 compared to that of the open chain[3,5] of 13/75. Unfortunately, the linear part is obtainable for small u^2-values only; both the ring molecule and the monodisperse open chain exhibit a significant upturn up to $u^2 = 4$ before the curves bend down to approach the u-symptote. The upturn is more pronounced for the ring molecule than for the open chain.

In *Figure 1* we also plot the deviation of the first cumulant from the correct value when the hydrodynamic pre-average approximation is used. The formula for $\Gamma_{\rm pre}$ is given by equation (15) with disregard of the second integral (or putting $a = \infty$)[9]. As for star-branched macromolecules $\Delta\Gamma/\Gamma$ exhibits a maximum at $u = 3$, and the error introduced by the pre-average approximation reaches values up to 17%. The maximum arises from the increased segment density in the ring molecule compared with that of the open chain[3].

Figure 3 shows the angular dependence of the first cumulant on the reciprocal particle scattering factor. The interdependence of the quasi-elastic and integrated scattering functions can be well represented by a semi-empirical relationship:

$$\Gamma/q^2D = P(q)^{-\nu} \qquad (30)$$

with exponents $\nu_{\rm ring} = 0.485$ and $\nu_{\rm chain} = 0.526$. Both curves have a slight curvature at small values of $P(q)$ which would be scarcely detectable in experiments. The simple semi-empirical relationship of equation (30) is thus useful

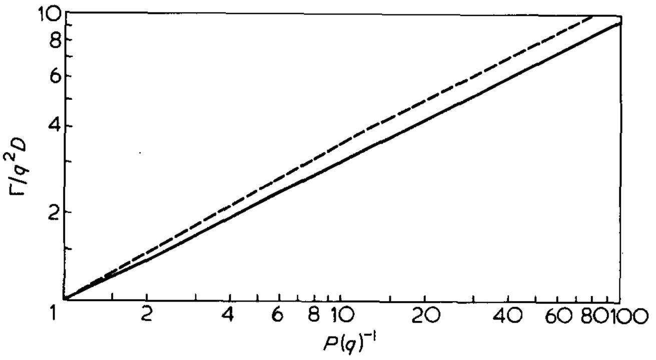

Figure 3 Interdependence of the normalized first cumulant and the particle scattering factor (normalized static structure factor) for ring (———) and chain (— — — —) molecules

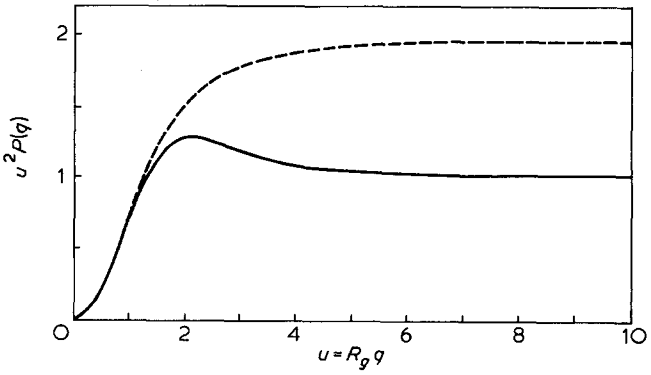

Figure 4 Asymptotic behaviour of the particle scattering factors of ring (———) and chain (— — — —) molecules in the Kratky plot

for experimental differentiation between the behaviour of a ring and an open chain. Appropriate use of equation (30) can be made, however, only if both functions Γ and $P(q)$ are measured accurately enough; and this requires, if any possible, the simultaneous recording of the integrated and quasi-elastically scattered intensities.

Miscellaneous structure-dependent quantities

In this last section we give a collection of various quantities which can be obtained from experiments and which allow distinctions between a ring and an open chain.

By direct comparison of the ring with the open chain at the same degrees of polymerization, we can obtain the geometric shrinking factor g_{ring} and the hydrodynamic factor h_{ring} due to Zimm and Stockmayer[6] and Kurate and Fukatsu[12]:

$$g_{\text{ring}} = \frac{\langle S^2\rangle_{\text{ring}}}{\langle S^2\rangle_{\text{chain}}} = 1/2 \tag{31}$$

$$h_{\text{ring}} = \frac{D_{\text{chain}}}{D_{\text{ring}}} = 8/(3\pi) = 0.84882 \tag{32}$$

More interesting than these two quantities is the S/R–factor defined as $S/R = \langle R_h^{-1}\rangle\langle S^2\rangle^{1/2}$. This quantity is independent of bond length, and does not directly depend on the number of bonds N. Also, the effect of excluded volume can be expected to cancel to a large extent. The hydrodynamic radius is defined as:

$$\langle R_h^{-1}\rangle = 6\pi\eta_0 D/k_b T \tag{33}$$

One finds for the rings in the unperturbed state:

$$(S/R)_{\text{ring}} = (\pi/2)^{1/2} = 1.2533 \tag{34}$$

while for the chain:

$$(S/R)_{\text{chain}} = 8/3\pi^{1/2} = 1.508 \tag{35}$$

If the effect of excluded volume is taken into account one has, in the region of validity of the cluster expansion[7,12,14]:

$$(S/R)_{\text{ring}} = 1.2533\,\frac{1+0.7854z}{1+0.630z} = 1.2533(1+0.1554z) \tag{36}$$

$$(S/R)_{\text{chain}} = 1.508\,\frac{1+0.638z}{1+0.609z} = 1.508(1+0.029z) \tag{37}$$

The utility of the quantity S/R is that the ring can be differentiated from the open chain by scattering measurements from a ring molecule only, and measurement of the corresponding open chain is not needed. This property is of great value, particularly when biological material is considered where the corresponding open chain may be difficult to obtain.

Finally, we give in *Figure 4* a representation of the integrated scattering function in the Kratky plot, i.e. $u^2P(q)$ against u. In contrast to the open chain, there is a maximum at $u = 2.15$ for the ring molecule and an asymptote, $u^2P(q) \to 1.00$, which is half that of the open chain. This behaviour could also make characterization of a ring molecule easy, if $P(q)$ could be measured to large enough q-values.

ACKNOWLEDGEMENTS

This work benefitted greatly from discussions with Professor Walter H. Stockmayer, Dartmouth College, Hanover, USA, during his stay at our laboratory. We are most grateful for his comments. We also thank Professor Z. A. Akcasu, Ann Arbor, USA, for discussion of his unpublished results[9]. Financial support of this project by Deutsche Forschungsgemeinschaft is gratefully acknowledged.

REFERENCES

1 Akcasu, Z. and Gurol, H. *J. Polym. Sci., Phys. Edn.* 1976, **14**, 1
2 Burchard, W. *Macromolecules* 1978, **11**, 455
3 Burchard, W., Stockmayer, W. H. and Schmidt, M. Submitted to *Macromolecules*
4 Schmidt, M. and Burchard, W. *Macromolecules* 1978, **11**, 460
5 Burchard, W., Schmidt, M. and Stockmayer, W. H. Submitted to *Macromolecules*
6 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 1301
7 Casassa, E. F. *J. Polym. Sci. A.* 1965, **3**, 605
8 Abramowitz, M. and Stegum, I. A. 'Handbook of Mathematical Functions', Dover Publishers, New York, 1970, Table 7.5, p319
9 Akcasu, Z., Benmouna, M. and Han, C. C., Personal Communication *Polymer* 1980, to be published
10 Ptitsyn, O. B. *Zh. Tekhn. Fiz.* 1959, **29**, 75
11 Bloomfield, V. A. and Zimm, B. H. *J. Chem. Phys.* 1966, **44**, 315
12 Fukatsu, M. and Kurata, M. *J. Chem. Phys.* 1966, **44**, 4539
13 Yu, H. and Fujita, H. 1972, quoted in ref 15
14 Stockmayer, W. H. and Albrecht, A. C. *J. Polym. Sci.* 1958, **32**, 215
15 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971