Dimensional Description of Cyclic Polymers

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Cyclic structures are often used to model and simulate long chain molecules due to the simplification of no chain end effects. Further, many technically important and biologically relevant molecules are cyclics. In this letter, a dimensional analysis of cyclic polymers and its use to describe scattering data from cyclic macromolecules is presented. The validity of the new approach to describe cyclic structures is demonstrated and the Casassa form factor previously used for cyclic polymers is critically revisited.

Introduction.- Cyclic structures are prevalent in many biological and synthetic molecules; e.g. cyclic molecules play an important role in the DNA transcription process [1] as well as complex biochemical processes like insulin secretion [2]. Synthetic systems like macrocyclic-ethers (crown-ethers) have been synthesized for specific applications like cationic and anionic complexation agents [3]. The absence of chain ends has led to speculation that the dynamic properties of polymeric rings differ from their linear analogues [4]. Detailed experimental studies have been conducted on cyclic *poly(dimethyl siloxane)* (PDMS) [5-7] due to its natural tendency to form rings. Small angle neutron scattering (SANS) has been a primary tool to quantify these structures, and has made it possible to corroborate theoretical/computational predictions regarding the structure/conformation of ring polymers under different thermodynamic conditions. These studies along with the recent development of Ru-based catalyst system by Bielawski et al. [8] for industrial scale production of cyclic polymers has invigorated interest in obtaining effective descriptions of cyclic structures.

SANS is an effective analytic technique to characterize local features of the structure like the mean square radius of gyration of the cyclic polymer molecule, R_g, as well as the mass/size scaling of such a structure. The Casassa form factor [9] has been used for cyclic macromolecules. It has been reported in literature that the Casassa equation [9] results in less than satisfactory fits to describe the observed small angle scattering (SAS) patterns [5], especially for larger rings of higher molar mass.

This letter describes a pathway to model cyclics using a new approach developed by Beaucage [10, 11] for analyzing hierarchical structures. We shall also look at existing SANS data of cyclic polymers from the literature as a check for this approach [10, 11]. It will be evident that this model yields an effective description for cyclic polymers. Additional information regarding the conformational state of the cyclic structures as well as their thermodynamic state can be understood using this approach. The final section will critically assess the Casassa equation [9, 12] using the new structural model.

Scaling and model for cyclic structures.- Any hierarchical molecular structure can be assumed to be composed of z primary units, of which p units describe the *minimum* or *short circuit* path through the structure (broken line and lighter circles in FIG. 1); $(z - p)$ units are present in structural branches, so the branch fraction ϕ_{br} is then given as [10],

$$\phi_{br} = \frac{z - p}{z} \tag{1}$$

Quantitative ϕ_{br} estimates can be obtained for a variety of different architectures [10, 11]. Detailed information regarding the structure of hierarchical/branched materials can be obtained from SAS data ϕ_{br} analysis [10, 11]. Additional information regarding structure can be obtained from dimensional parameters obtained from such an analysis. The mass fractal dimension, d_f, often describes the average structure of such hierarchical materials. The SAS analysis given by Beaucage [10] results in additional parameters, viz. the minimum path dimension, d_{min}, and the connectivity dimension, c. These dimensions reflect different attributes of a hierarchical structure. The connectivity dimension reflects topology [10, 11] since,

$$z = p^c \tag{2}$$

d_{min} reflects the tortuosity of the minimum path often dictated by the thermodynamics of macromolecular systems [10, 11],

$$p = R^{d_{\min}} \tag{3}$$

where R could be some average measure of size for the overall structure like the polymer coil radius of gyration, R_g. This approach decomposes the overall structure as reflected by d_f, into contributions from topological and tortuosity effects as [10, 11],

$$d_f = cd_{\min} \tag{4}$$

We can adopt this model to describe a cyclic structure. The minimum path for any structure is the path of conductance (the path traversed to get across the structure in space). This feature of the minimum path for a cyclic structure is shown schematically in FIG. 1. As can be seen in FIG. 1, the minimum path for a cyclic structure would be composed of half its length ($p = z/2$); so from equation 2,

$$c = \ln(z) \big/ \ln(z/2) = \ln(z) \big/ \left(\ln(z) - \ln(2)\right) \tag{5}$$

c is a function of z and approaches 1 (the definition of a linear chain) for high z. The primary particles which do not compose the minimum path contribute toward ϕ_{br}. Hence in theory, for cyclic structures ϕ_{br} should display a constant value of 0.5 (FIG. 1), regardless of molar mass, z.

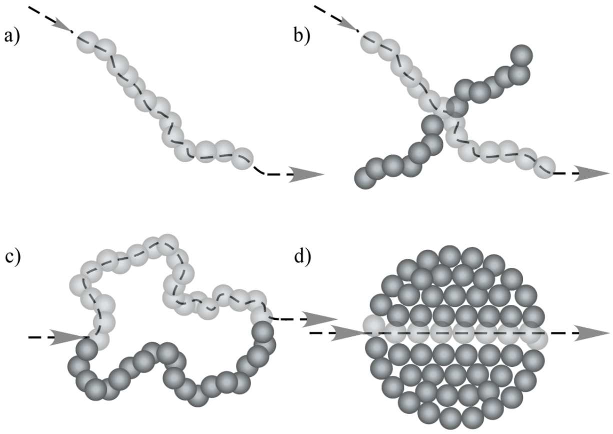


FIG. 1. Schematic representation of the minimum path, p, through a cyclic structure (1c) as discussed in text. The minimum path for a cyclic would constitute half the chain (indicated by the broken line and lighter circles); a) linear chain, b) 4-arm star, c) cyclic, d) disc.

Small angle neutron scattering.- The scattering curve from a mass-fractal object like a cyclic displays two regimes, at low-q (Guinier's law) [10, 11],

$$I(q) = G\exp\left(\frac{-q^2R_g^2}{3}\right) \tag{6}$$

and at high-q (power law) [10, 11],

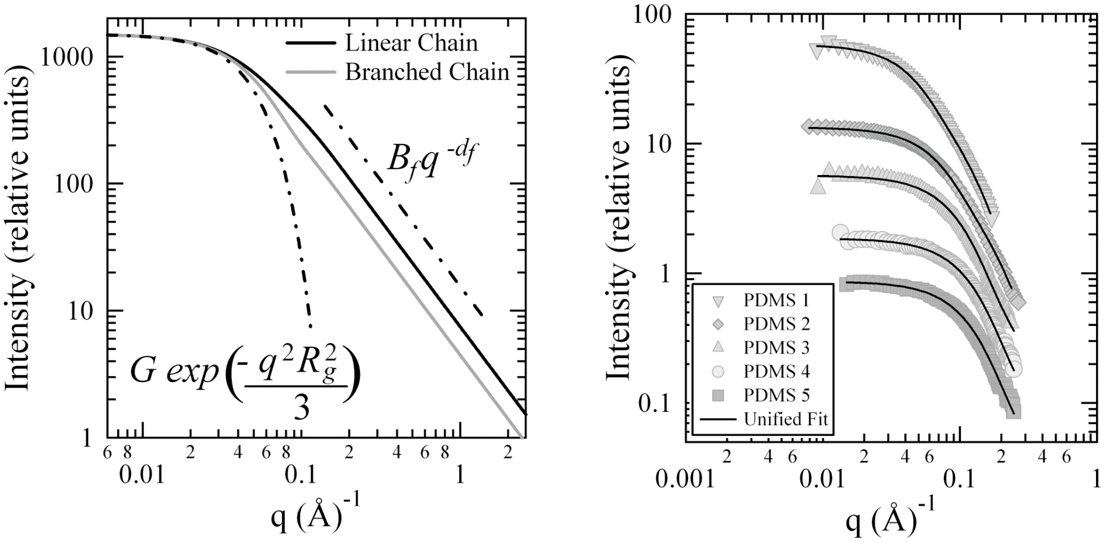
$$I(q) = B_f q^{-d_f} \tag{7}$$

where I is the scattered intensity, q is the scattering vector given as $q = 4\pi\sin(\theta/2)/\lambda$ (θ: scattering angle, λ:wavelength of the radiation), G and B_f are the Guinier and power law prefactors respectively. FIG. 2a shows the four parameters that can be obtained from SANS data, the Guinier prefactor G, the radius of gyration of the polymer coil R_g, the power law prefactor B_f, and the mass-fractal dimension d_f. G and R_g are derived from Guinier's law (equation 6), which predicts an exponential decay in scattered intensity at the R_g of the structure, and B_f and d_f reflect the power law which gives the mass/size scaling of the structure in terms of the mass-fractal dimension d_f (equation 7). Beaucage [10] has shown that topology of the structure can be quantitatively estimated from such SANS data; d_{min} for example can be calculated as [10],

$$d_{\min} = \frac{B_f R_g^{d_f}}{G\left(\Gamma^{d_f/2}\right)} \tag{8}$$

where Γ is the gamma function. Also shown in FIG. 2a is the signature effect of the topological structure on SANS data. The black curve represents SANS from a linear structure for which $z = p$, $d_{min} \sim d_f$ and $c = 1$. The grey curve represents scattering from a more compact structure for which $z >> p$, $d_{min} \sim 1$, and $c \sim d_f$. Topology is thus reflected by the shift of power law relative to the Guinier's law in SANS data, and is quantifiable (equation 8).

SANS data from blends of hydrogenous and deuterated cyclic PDMS, digitized from the literature works is shown in FIG. 2b [5-7]. The details of the PDMS samples are given in Table I. The SANS data are fit to the unified function [13] and the dimensions associated with ϕ_{br} from these fits are tabulated in Table I. According to the random phase approximation the structure factor for a binary blend of hydrogenous (H) and deuterated (D) components would be a function of the individual structure factors, $S_H(q)$ and $S_D(q)$ the structure factors for the hydrogenous and deuterated components respectively and χ_F, the Flory-Huggins interaction parameter [14]. There are two assumptions involved in the unified fits [13] performed on the SANS data. Firstly we assume that the blends of hydrogenous and deuterated PDMS constitutes an athermal mixture where $\chi_F = 0$ and the individual structure factors have the same functional form ($R_{g,H} \approx R_{g,D}$) and hence that the data can be fit using a single structure factor $S(q,R_g)$. Calculation of ϕ_{br} requires structural information from two levels; the overall chain size and the persistence length. Since these SANS data sets do not cover the necessary q-range, the size of the primary building blocks is used from literature value of persistence length for PDMS of 5.61 Å [15]. The ϕ_{br} values for all the cyclic samples calculated in this way from unified fits [13] are close to 0.5 (Table I). It is also of interest to note the values of the minimum path dimension, d_{min}. For a conventional branched polymer, like long chain branched polyethylene, d_{min} should reflect the scaling of a linear chain in similar thermodynamic conditions [11]. For example, in dilute good-solvent conditions, the value of d_{min} should approach good-solvent scaling of a linear chain of 5/3, and in the melt, it should approach Gaussian linear chain scaling of 2.



a) b)

FIG. 2. a) Representation of small angle neutron scattering data from hierarchical linear (black curve) and branched (grey curve) structures, b) Digitized small angle neutron scattering data from blends of hydrogenous and deuterated cyclic PDMS samples from literature [5-7]. The details of the samples are given in Table I. The data is fit to the unified function [13].

In the context of this scaling model it is interesting to compare a 4-arm star (monodisperse arm lengths) and a cyclic polymer, since both these structures display ϕ_{br} = 0.5. This is indicated schematically in FIG. 1b and 1c. For a melt of a 4-arm star polymer, d_{min} = 2 (the scaling of a linear chain in the melt state). In the case of a cyclic polymer melt, due to the constraints of the chain ends being confined, we expect d_{min} to approach 2 for large cyclics in the melt as the conformational constraint is reduced.

Table I. Details of polydimethylsiloxane (PDMS) samples from literature [5-7]. M_w: weight average molar mass of H/D components. The unified function [13] fits to small angle neutron scattering data in FIG. 2b results in the following parameters: Guinier prefactor G, R_g, power law prefactor B_f, d_f, d_{min}, c, z and ϕ_{br}.

Sample	M_w (g/mol)[5-7]	G	R_g (Å)	B_f	d_f	d_{min}	c	z	ϕ_{br}
PDMS 5[5]	5,000/5,000	3.9	13.6	0.0214	2.11	1.37	1.54	6.5	0.48
PDMS 4[7]	4,780/4,760	3.9	13.6	0.0210	2.12	1.39	1.52	6.5	0.48
PDMS 3[5]	4,780/11,140	5.6	16.8	0.0185	2.16	1.51	1.43	10.6	0.50
PDMS 2[6]	8,900/11,110	6.2	20.3	0.0183	2.07	1.54	1.35	14.3	0.49
PDMS 1[6]	19,800/16,300	12.6	30.6	0.0155	2.11	1.72	1.23	35.9	0.48

As can be seen from the values listed in Table I, d_{min} increases with increasing molecular weight of the cyclic PDMS blends from 1.37 to 1.72, asymptotically approaching the mass/size scaling of a linear chain in the melt (Gaussian, $d_f = 2$) [14]. The observed values of d_{min} (Table I) are much lower than 2, due to constraining the ends of the chain. d_{min} values for the cyclic PDMS blends are plotted against the degree of polymerization, z (Table I), in FIG. 3. The filled circles are the actual d_{min} values from fits shown in FIG. 2b. The broken line in FIG. 3 represents the calculated curve for projected values of d_{min} for higher z, under the constraint of $\phi_{br} = 0.5$. The exact relationship used to calculate the forecasted d_{min} curve can be obtained from the definition of ϕ_{br} (equation 1) and $p = z/2$ [10], and is given as,

$$d_{\min} = d_f \left(1 + \frac{\ln(\phi_{br})}{\ln(z)} \right) \tag{9}$$

As can be seen from FIG. 3, for $\phi_{br} = 0.5$ for cyclics, and $d_f = 2$, at very large size and molecular weight, the projected d_{min} value asymptotically approaches 2, indicating the approach to a linear chain in the Gaussian state for infinite molecular weight cyclics [14]. The scaling model is thus capable of accounting for the expected behavior of a cyclic chain. As was discussed in the previous paragraph, d_{min} for a cyclic polymer melt would always be lower than 2, and the actual values from the SANS fits, and the projected behavior (equation 9) corroborate this.

The minimum path dimension, d_{min}, mimicking the dimension of the linear path through the structure has also been reported for long chain branched macromolecules [10] and hyperbranched polymers [11] under different thermodynamic conditions. For cyclic polymers, d_{min} could be used as a parameter to probe the conformation attained under different conditions, like in melts and solutions. For example, a dilute solution of cyclic polymers in a solvent would be characterized by d_{min} values asymptotically approaching good solvent scaling for linear chains of 5/3 at high molar mass [14].

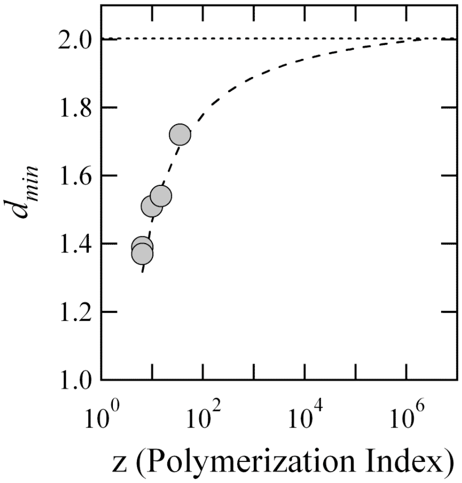


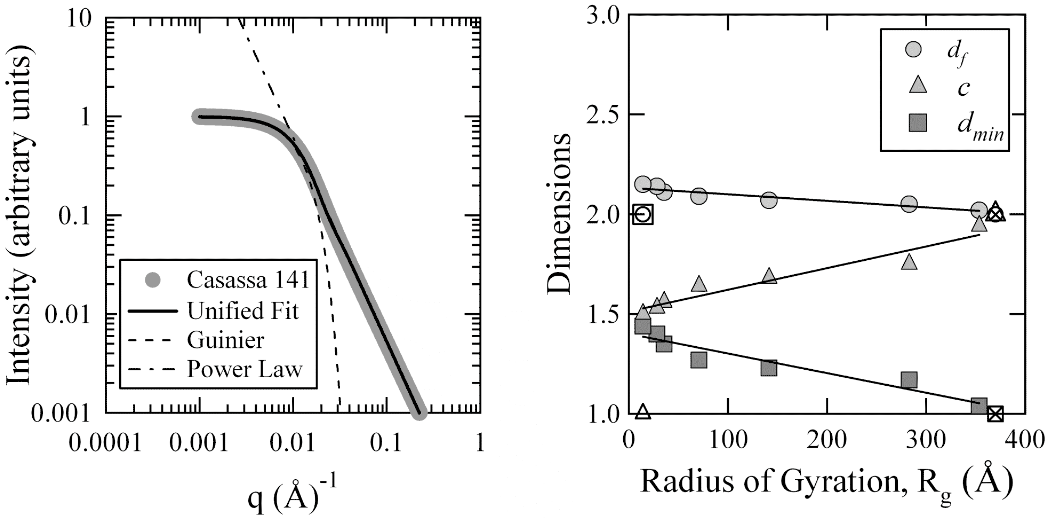
FIG. 3. Minimum path dimension, d_{min}, plotted as a function of the polymerization index, z. The filled circles are the actual d_{min} values from Table I. The broken line represents calculated d_{min} at higher z values from equation 9 assuming $d_f = 2$ and $\phi_{br} = 0.5$.

Casassa equation.- The Casassa equation [9] gives the scattering form factor for a cyclic/ring polymer, and has been widely used in literature reports concerning small angle scattering from cyclic structures [5, 6]; though it has been found to be of limited use as a fitting function to actual SANS data. The Casassa form factor [9] is given by,

$$P(q) = \frac{2}{\sqrt{t}} \exp\left(\frac{t}{4}\right) \int_0^{t^{1/2}/2} \exp\left(x^2\right) dx \qquad (10)$$

where $t = q^2 R_g^2$. The product of the exponential and the integral in equation 10 is also known as the Dawson integral [9]. As reported in literature [5, 6], the Casassa equation does not accurately predict actual scattering data from cyclics, especially for higher molecular weight cyclics [5, 6]. Some authors have used the Debye function [16] for linear polymer chains to attempt to fit cyclic scattering data with equally poor results. The failure of the Debye equation [5, 6] as a fit to SAS data from cyclics is not surprising, since the Debye equation describes linear Gaussian polymer chains [16]. The unsatisfactory fits obtained using the Casassa equation, according to the authors of these reports [5, 6] is possibly related to contamination of these samples with linear chains. We believe that a more fundamental problem exists with the Casassa equation as outlined below.

Unified function and ϕ_{br} analysis.- A calculation based on the Casassa function is shown in FIG. 4a for a cyclic with R_g = 141 Å and the calculated Casassa form factor is fit to the unified function [13]. The distinct knee feature in this curve is a clear indication of a high value of ϕ_{br} and a dense structure (see FIG. 2a). The unified function [13] results in the fit parameters: the mass fractal dimension d_f; the power law prefactor, B_f; the Guinier prefactor, G; and the radius of gyration, R_g, which can be used to calculate ϕ_{br}, d_{min}, and c [10, 11].



a) b)

FIG. 4 a) Unified function [13] fit to the calculated Casassa form factor. The distinct knee feature is a clear indication of a dense structure with a high value of ϕ_{br} as predicted by the model and, b) Mass fractal dimension, connectivity dimension, and minimum path dimension, plotted as a function of the radius of gyration of calculated Casassa form factors. These dimensions were obtained by unified function [13] fits similar to that shown in FIG. 4a. Open symbols represent dimensions for a linear Gaussian chain, crossed open symbols represent a 2-d disc.

An analysis of the dimensions obtained from the unified fits [13] from multiple calculated Casassa form factors indicates the probable reason for problems encountered in using the Casassa equation as a fitting function for higher molecular weight cyclics. In FIG. 4b, the different dimensions are plotted as a function of the cyclic R_g. With increasing size of the cyclic molecule, the connectivity dimension, c, tends to d_f and to 2, and the minimum path dimension, d_{min}, tends to 1 (FIG. 4b). The Casassa equation reduces to a 2-d disc scattering function at high molecular weight rather than an asymptotic approach to a linear chain: this could be an explanation of the problems encountered in the literature of using the Casassa equation as a fitting function to SANS data from cyclic macromolecules [5, 6]. The Casassa approach considers a Gaussian distribution of the segments which make up the structure between any two points, for the conditions that the start and end units of the chain are the same unit and that the overall structure is two dimensional. At high molar mass these conditions can only be met by a disk.

In context of the scaling model the validity of the Casassa approach is doubtful, since it is based on the constrained cyclic structure ($d_{min} < 2$) being described in the framework of Gaussian distribution of individual segments ($d_{min} = 2$). On the other hand, the model for cyclic structures presented here (FIG. 1c), makes no assumption concerning the dimensionality of the structure. The only assumption in the scaling model is that the minimum path, $p = z/2$. This constraint is equally valid for a symmetric 4 arm star polymer, however, the 4 arm star requires a further constraint that d_{min} is fixed by the thermodynamic conditions to either 2 for a melt or 5/3 for good solvent conditions. So in the scaling model, the conformational constraint of FIG. 3 defines a cyclic macromolecule.

Conclusions.- A new scaling model for cyclic polymers was presented and applied to literature SANS data. The new analysis procedure can characterize fundamental structural and thermodynamic features associated with cyclic macromolecules. It was demonstrated that cyclic structures, regardless of their size and molar mass, can be characterized by $\phi_{br} = 0.5$ as predicted by the model. This approach results not only in an effective description of the cyclic structures in general, but also pin-points problems with traditional approaches in the literature, viz. the Casassa form factor [9]. With the advent of new catalyst systems for the synthesis of cyclic polymers on an industrial scale [8], this scaling approach could result in a new and effective route to obtain routine characterization of these structures. It is also hoped that this approach could be used to further our understanding of a variety of cyclic structures encountered in biomolecules as well as synthetic cyclic molecules.

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