

# Role of cyclization in the degree-of-polymerization distribution of hyperbranched polymers

## Modelling and experiments

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Received: 4 December 1998/Revised version: 17 February 1999/Accepted: 17 February 1999

## Summary

A kinetic model of formation of hyperbranched polymers by step polyaddition of a  $BA_f$  monomer including cyclization was developed. Reactions between acyclic-acyclic and acyclic-cyclic molecules and cyclization within acyclic molecules were considered. For cyclization within isomers of an  $x$ -mer, a bridging function between linear and spherical structures was used. Fractions of cyclic  $x$ -mers are predicted to increase with increasing degree of polymerization  $x$  and overall conversion of B groups. High fractions of cyclics were found in poly[2,2-bis(hydroxymethyl)propanoic acid] (poly (dimethylolpropionic acid)) by mass spectroscopy (ESI/FT MS) in a reasonable agreement with the model.

## Introduction

Functional hyperbranched polymers and dendrimers are polymer network precursors of compact architecture. While dendrimers are monodisperse, hyperbranched polymers exhibit a (broad) distribution of degrees of polymerization. These polymers and their special features have been reviewed in the literature (cf., e.g., (1-5)). The hyperbranched polymers are formed from  $BA_f$  monomers, where groups A and B react to give bond A-B. The hyperbranched polymers are characterized not only by a wide distribution of degrees of polymerization but also by distribution of shapes, ranging from purely linear to purely spherical through abundant intermediate structures. Several ways of controlling the molecular weight and shape distribution have been proposed or employed, such as addition of a core (an  $A_f$  monomer), controlled monomer feed, or variable reactivities of A groups. In the majority of quantitative considerations, only the *intermolecular reaction* between the A and B groups was considered. Under these conditions, every molecule, whatever its size, is treelike and bears one unreacted B group and  $x(f - 1) + 1$  unreacted A groups. It has been realized that *intramolecular reaction* within groups of the same molecule can occur but it was considered to be relatively unimportant because only one ring can be formed.

*Simulations of hyperbranched polymers.* The ring-free step polyaddition of a  $BA_f$  monomer was first treated by Flory (6) who used a combinatorial method falling within the category of *statistical* branching theories (cf., e.g., (7,8)). The statistical approach has been substantially extended in the available structural information (higher MWD moments, free-functionality distributions, effect of differences in reactivity, addition of a core, etc.) by using the *theory of branching processes* employing the formalism of cascade substitution and generating functions (cf., e.g., (9, 10); a more detailed treatment will be published). These approaches show that for  $f > 1$  both the number- ( $P_n$ ) and weight-average ( $P_w$ ) degrees of polymerization diverge if the conversion of B groups,  $\alpha_B$ , goes to completion and that the polydispersity  $P_w/P_n$  also diverges. The statistical theories, strictly speaking, describe the situation when the structure is controlled by equilibrium.

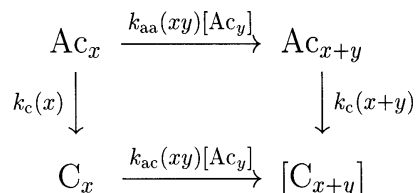
For kinetically controlled reactions, the structure development can be described by a set of kinetic differential equations for time change of each distinguishable species (molecule) which can be solved either analytically (cf. (11)) or numerically by the moment method. Monte-Carlo simulation of this process is another alternative ( $10^6$ - $10^8$  monomer units) for solution which offers the whole distribution and is applicable also to cases where the moment method fails (12, 13). Non-mean-field effects arising from molecular-size-dependent factors (steric obstruction, diffusion) or history-dependent effects (staging) can also be taken into account (14, 15). Monte-Carlo simulation of a ring-free reaction of  $BA_f$  was performed by Hanselmann et al. (16) using 500-5000 monomer units.

Simulation of build-up of dendrimers and hyperbranched molecules in space has also been performed. While simulation of single dendritic structures is relatively straightforward (17, 18), simulation of distributions is more difficult because of limitations imposed on the number of units employed. Recently, Widman and Davies (19) used the rotation-isomeric-state Metropolis Monte-Carlo simulation with exclusion of steric effects and Aerts (20) the bead-spacer model used by Mansfield and Klushin (18). In neither case, cyclization reaction was considered. Cyclization during the reaction of an  $BA_2$  monomer was modelled on a lattice (60 x 60 x 60 lattice sites), where bonds can connect a unit to any of its 26 neighbors, is (21). For certain dendrimers, cyclization was studied (22, 23) both experimentally and theoretically (molecular mechanics force field model (23)).

In this work, we developed a kinetic model in which cyclization was taken into account. The results are compared with evolution of distributions of acyclic and cyclic species in poly[2,2-bis(hydroxymethyl)propanoic acid] which were determined by electrospray ionization Fourier-transform mass spectrometry (ESI/FT MS).

## Results and Discussion

*Kinetic simulation of acyclic and cyclic molecules.* Formation and transformation of acyclic and cyclic molecules are described by the following scheme:



where  $Ac_x$  and  $C_x$  represent an  $x$ -mer which is acyclic and contains one cycle, respectively. A cyclic molecule can react with an acyclic one, but two cyclic molecules cannot react because none of them has an unreacted B group.

For the intermolecular reactions between two monomers, between monomer and a cyclic or acyclic molecules, between two acyclic molecules, or between an acyclic and a cyclic molecule, a second-order reaction has been assumed. As for catalyzed reaction kinetics, the reaction rate of the specific molecules was proportional to the product of their 'concentrations' (probability densities; for details, cf. (12-14)). The weightings for selection of the molecules for intermolecular reactions are determined by the numbers of unreacted groups in reacting molecules which determine the number of ways the two selected molecules can react. Equal reactivity of groups was assumed in the simulation runs shown here.

The reaction scheme given above is described by the following differential equations

$$\frac{d[Ac_x]}{dt} = \left(\frac{1}{2}\right) \sum_{j=1}^{x-1} k_{aa}(j, x-j)[Ac_j][Ac_{x-j}] - [Ac_x] \sum_{j=1}^{\infty} k_{aa}(x, j)[Ac_j] - [Ac_x] \sum_{j=1}^{\infty} k_{ac}(x, j)[C_j] - k_c(x)[Ac_x] \quad (1)$$

$$\frac{d[C_x]}{dt} = k_c(x)[Ac_x] + \left(\frac{1}{2}\right) \sum_{j=1}^{x-1} k_{ac}(j, x-j)[Ac_j][C_{x-j}] - [C_x] \sum_{j=1}^{\infty} k_{ac}(j, x)[Ac_j] \quad (2)$$

where

$$\begin{aligned} k_{aa}(j, x-j) &= k[x(f-1) + 2] \\ k_{aa}(x, j) &= k[(x+j)(f-1) + 2] \\ k_{ac}(j, x-j) &= k[(x-j)(f-1)] \\ k_{ac}(x, j) &= k[j(f-1)] \end{aligned}$$

$k$  [conc.<sup>-1</sup> time<sup>-1</sup>] is a rate constant for the reaction of A and B group and  $[Ac_x]$  and  $[C_x]$  are concentrations of acyclic and cyclic  $x$ -mers, respectively.

Weightings for the cyclization reaction, determined by  $k_c$ , are complicated due to (1) the existence of distribution of isomers of an  $x$ -mer and (2) associated functional complexity of the probability that two groups in the same molecule can come close to each other to form a bond. We have applied the Significant Structure Approach used in the thermodynamics of mixtures of liquids (24,25). In this approach, the weighting factor for the cyclization in an  $x$ -mer is taken as a weighted average over two limiting structures: a linear molecule and a spherical one with one B group in the extreme shell in generation  $g$  (bridging function) (examples of possible structures are shown in Figure 1).

The derivation given here represents only the first approximation and will be discussed in more detail elsewhere. For the linear isomer, a B group located anywhere along the chain is considered to react with any A group along the chain with the limitation

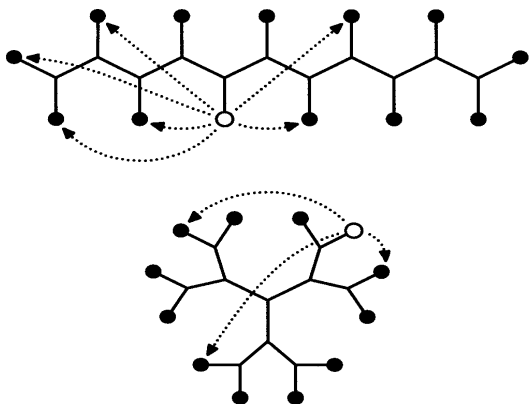


Figure 1: Extreme structures of a hyperbranched  $x$ -mer and possible cyclization reactions

by the smallest possible ring of size  $i_0$ . The Stockmayer-Jacobson scaling for the probability of forming a ring of size  $x$ ,  $P_c(x) \propto x^{-3/2}$ , is used. Summation over all possible locations of B groups and ways of ring formation gives the following equation

$$k_{c,\text{lin}}(x) = k \frac{2a(f-1)}{x} \sum_{i=i_0}^x (x-i+1) i^{-3/2} \quad (3)$$

$$a = \left( \frac{3}{2\pi q L^2} \right)^{3/2} \frac{1}{N_A} \quad (4)$$

(cf. (24)) where  $q$  is the number of monomer units in a statistical segment,  $L$  is the length per monomer unit, and  $N_A$  is Avogadro number. The cyclization probability for a spherically symmetric dendritic structure is derived considering the number of A groups at a distance  $g$  from the B group, counted in the number of generations. This number is multiplied by the accessibility factor. The accessibility factor is considered to decrease sharply with the distance because of the bulkiness of the spherical dendrite. The exponent  $\gamma(g)$  is semiempirical, satisfying this condition. The corresponding equation reads

$$k_{c,\text{dendr}}(g(x)) = ka(f-1) \sum_{i=1}^{g-1} f^{i-1} [(2i+1)s]^{-\gamma(i)} + (f+1)f^{g-1} [(2g+1)s]^{-\gamma(g)} \quad (5)$$

Here  $s = 1$ ; for  $i_0 > 1$ , this equation is coupled with equations

$$\gamma(j) = 3/2 + f^j/(j+1) \quad (6)$$

$$x = 1 + (f+1)(1 + f + f^2 + \dots + f^{g-1}) \quad (7)$$

The cyclization constant is obtained as an average:

$$k_c(x) = (k_{c,\text{lin}} + k_{c,\text{dendr}})/2 \quad (8)$$

because in the ideal case the populations of the extreme structures would be equal.

The cyclization intensity relative to intermolecular reaction is given by the dimensionless parameter

$$\Lambda = a/[BA_f]_0 \quad (9)$$

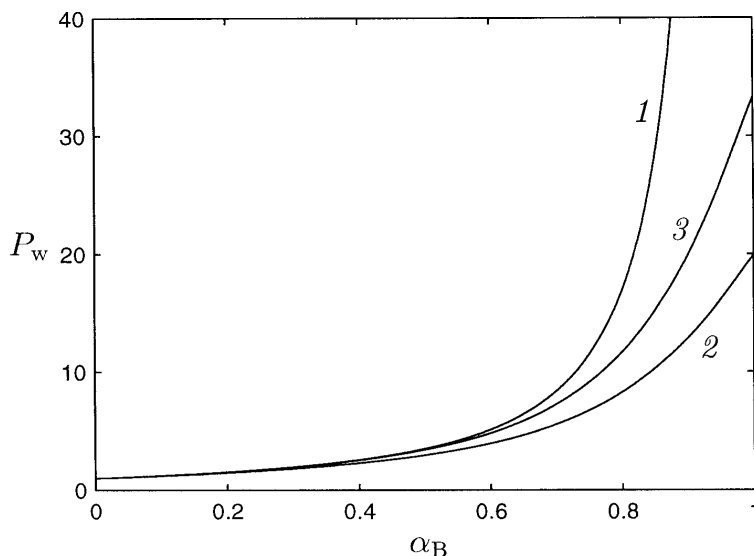


Figure 2: Weight-average degree of polymerization of a  $BA_2$  polymer in dependence on conversion of B groups  $\alpha_B$ ; 1 ring-free, 2,3 with cyclization, cyclization factor  $a = 1$ ,  $\Lambda = 0.1$ : 2  $i_0 = 1$ , 3  $i_0 = 2$

where  $[BA]_0$  is the initial concentration of monomer units.

Simulation of distributions composed of acyclic and cyclic molecules has been performed by Monte-Carlo simulation described in (12, 13). Examples of the simulation results are shown in Figures 2 and 3. The number- and weight-average molecular weights do not diverge but remain finite even at  $\alpha_B = 1$ . The final values depend on the degree of cyclization and also on the distribution of cycles among molecules of different sizes (Figure 2). Figure 3 shows a part of number-fraction distributions of acyclic and cyclic x-mers.

The following special features can be seen: (1) at a given conversion of B groups, the fraction of structures with a cycle (cyclics) increases with increasing molecular weight and converges to a certain value; (2) the fraction of cyclics increases with increasing conversion and converges to 100 % (all molecules are cyclics); (3) the extent of cyclization depends on the size of the smallest possible ring (in PDMPA, it is a dimeric ring,  $i_0 = 2$ , monomeric rings have not been detected).

*Comparison with experiment.* Samples of poly[2,2-bis(hydroxymethyl)propanoic acid] (poly(dimethylolpropionic acid), PDMPA)



were prepared by direct condensation using *p*-toluenesulfonic acid as a catalyst. Mass spectroscopic techniques in which only molecular ions are formed and observed (27) are powerful tools for distinguishing cyclized species (22, 23). Here, the Electrospray Ionization/Fourier Transform Mass Spectrometry (ESI/FT MS) was used. An example of the ESI/FT MS spectrum of PDMPA is shown in Figure 3.

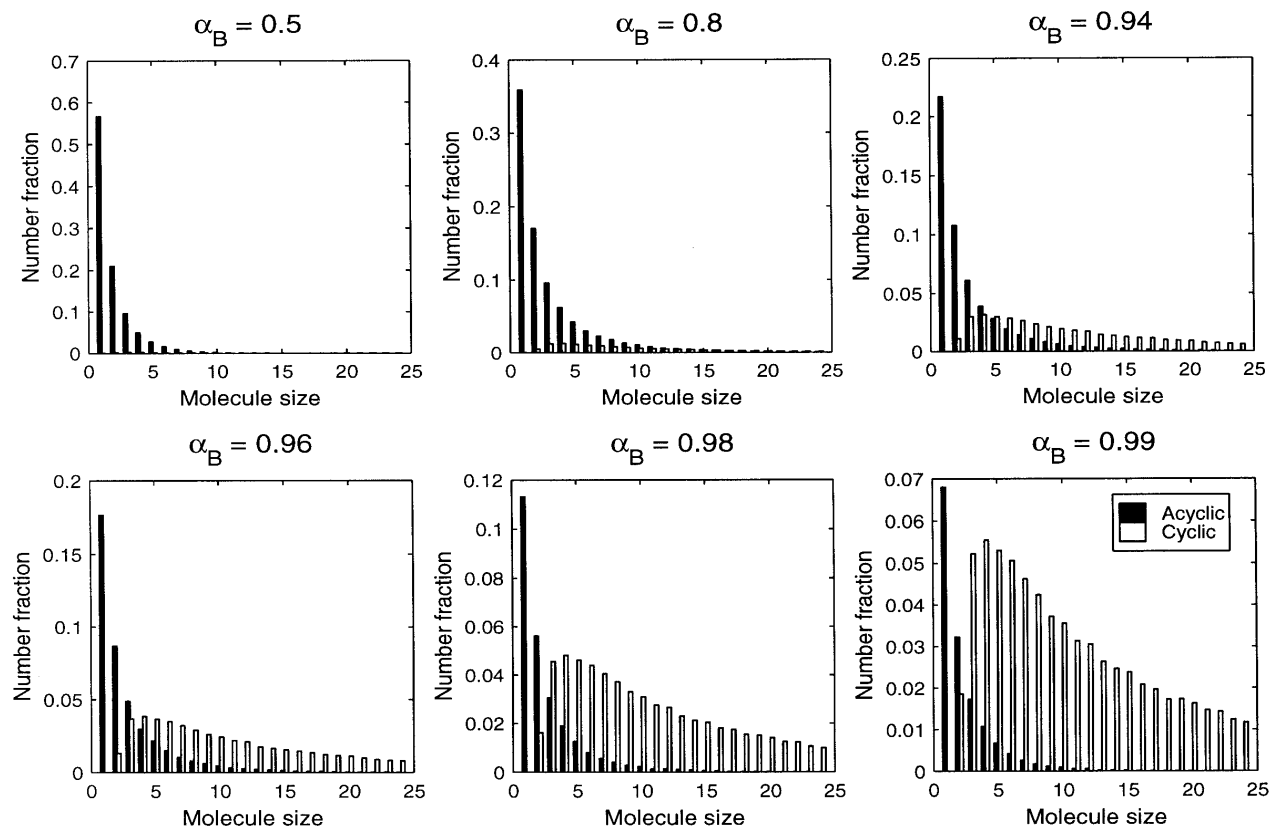


Figure 3: Examples of distribution of number fractions of acyclic (full bars) and cyclic (open bars)  $BA_2$   $x$ -mers for the conversion of B groups,  $\alpha_B$ , indicated; cyclisation intensity  $a = 1$ ,  $\Lambda = 0.1$ ,  $i_0 = 2$

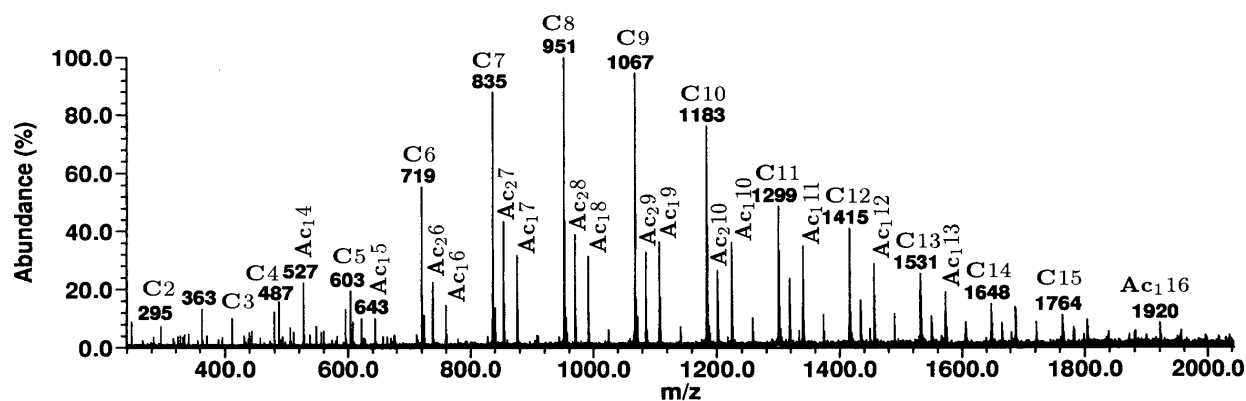


Figure 4: Example of ESI/FT MS record of sample of  $\alpha_B = 0.993$ , Na ionization;  $Ac_x$  = acyclic  $x$ -mer ( $Ac_1$  - Na salt (MW + 22 + 23),  $Ac_2$  - acid (MW + 23));  $C_x$  = cyclic  $x$ -mer (MW + 23)

In this paper, we do not compare the number-fraction distribution obtained by simulation and by ESI/FT MS but we limit the discussion to molar ratios of cyclics

$$n_{c,x} = \frac{[C_x]}{[Ac_x] + [C_x]}$$

Table 1: Molar fractions of cyclic molecules,  $n_{c,x}$ , in dependence on the degree of polymerization of PDMPA oligomers (calculated values for  $a = 1$  and  $\Lambda = 0.1$ )

$x$	$\alpha_B = 0.840$		$\alpha_B = 0.947$		$\alpha_B = 0.981$	
	experiment	theory	experiment	theory	experiment	theory
4	0.16	0.16	0.30	0.46	0.48	0.73
5	0.30	0.21	0.47	0.52	0.60	0.77
6	0.39	0.25	0.46	0.58	0.83	0.83
7	0.28	0.28	0.47	0.63	0.75	0.86
8	0.29	0.30	0.42	0.68	0.75	0.88
9	0.34	0.34	0.66	0.72	0.77	0.90
10	0.27	0.35	0.61	0.74	0.74	0.91
11	0.24	0.39	0.48	0.76	0.68	0.92
12	0.29	0.42	0.64	0.78	0.87	0.93
13	–	0.46	0.63	0.78	0.92	0.94

A comparison of data in Table 1 shows that predicted trends are obeyed. In view of the scatter of the experimental data, also the numerical agreement is reasonable. However, the observed increase in  $n_c$  with increasing  $x$  is generally flatter. This is apparently due to the simplifications used in the model; particularly the neglect of the fact that some of the B groups in compact molecules are heavily hindered and their reactivity severely restricted. The model will be further improved by considering this factor.

## Conclusions

Cyclization is an important factor in formation of hyperbranched molecules. It affects the reaction kinetics in that the cyclized molecules have no B group and can react only through their A groups. It was proved experimentally that the hyperbranched polyesters (PDMPA) are composed of a large fraction of cyclics. This fraction increases with increasing molecular weight of individual oligomers and increasing overall conversion of B groups. The results are in general agreement with the kinetic model that includes size-dependent cyclization.

## Acknowledgement

K.D. and J.S. wish to thank the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. A4050808) for support.

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