Simple models for complex polymers: hyperbranched polymers

K. Haydykivska and V.Blavatska

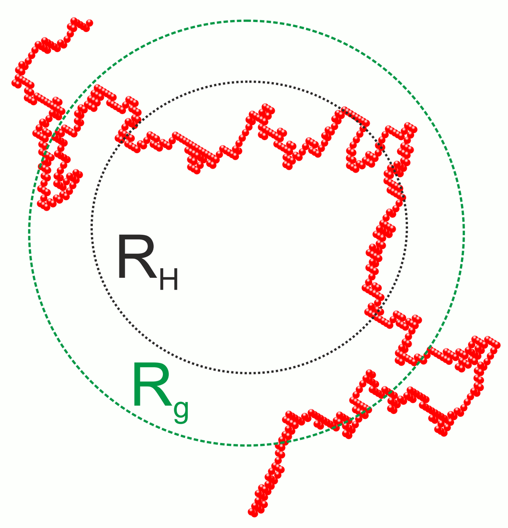
[1]Institute for Condensed Matter Physics of the National Academyof Sciences of Ukraine, Ukraine

Abstract

Many physical properties of polymer solutions strongly depend on the topology of the macromolecules. We study the size characteristics of a number of complex polymers by the means of Edwards model. All the chains are considered to be Gaussian thus allowing us to receive an exact expressions for gyration radius and hydrodynamic radius of the considered topologies. This model allows for an approximate description of the solution's properties in the vicinity of the θ-point. Here we concentrate on polymers with multiple branching points that form periodicstructures as well as some simple polymer networks.

Model and characteristics

~ Size characteristics



Gyration radius:

$$\langle R_g^2\rangle = \frac{1}{2S^2}\int_0^S\int_0^S \langle(\vec{r}(s)-\vec{r}(z))^2\rangle$$

Hydrodyramic radius:

$$\langle R_h^2\rangle^{-1} = \frac{1}{S^2}\int_0^S\int_0^S \langle|\vec{r}(s)-\vec{r}(z)|^{-1}\rangle$$

The averaging is performed with the partition function:

$$Z(\{S_i\}) = \int D\vec{r}(s)\prod_{i=1}^{f}\delta(\{\vec{r}_i\})\exp\left(-\sum_{i=1}^{f}H_i\right)$$

where H_i is an effective Hamiltonian of the ith strand: $H_i = \frac{1}{2}\int_0^{S_i}\left(\frac{\mathrm{d}\vec{r}_i(s)}{\mathrm{d}s}\right)^2$ and delta functions define the connection between them. Within the continuous chain model size characterisctics are calculated using the identities:

$$\langle(\vec{r}(s)-\vec{r}(z))^2\rangle = -2\frac{d^2}{d\vec{k}^2}\exp(-\iota\vec{k}(\vec{r}(s)-\vec{r}(z)))|_{\vec{k}^2=0}$$ for the gyration radius and

$$|\vec{r}(s)-\vec{r}(z)|^{-1} = (2\pi)^{-d}\pi^{\frac{d-1}{2}}2^{d-1}\int d\vec{k}\,k^{1-d}\Gamma\left(\frac{d-1}{2}\right)\mathrm{e}^{\iota\vec{k}(\vec{r}(s)-\vec{r}(z))}$$ for the hydrodynamic

Both characteristics are governed by the same scaling law $\langle R^2\rangle \sim S^{2\nu}$

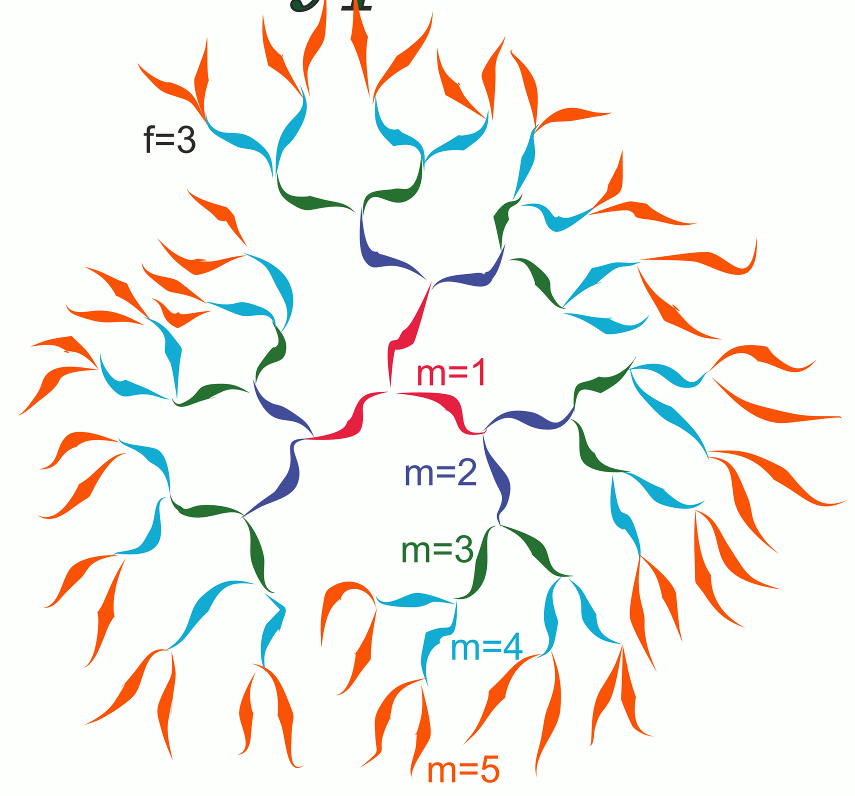
des Cloizeaux J. and Jannink G., Polymers in Solutions: Their Modelling and Structure, Oxford: Clarendon Press 1990.
K.Haydukivska, V.Blavatska, J.Paturej, Sci Rep, 2020, vol.10, p.14127;

~ Universal size ratio

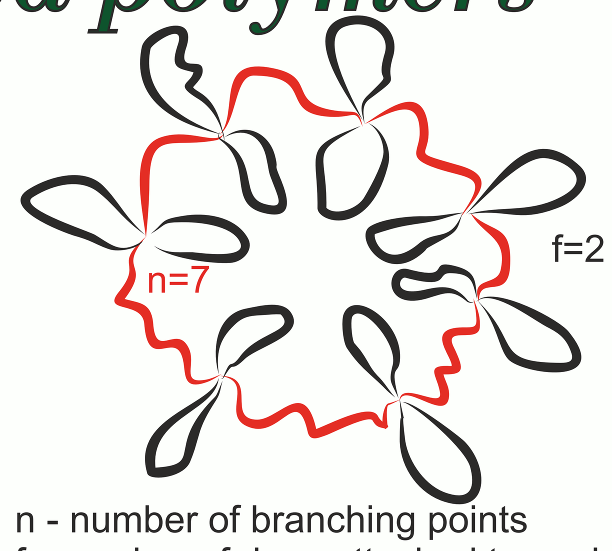
$$g = \frac{\langle R^2_{g,branched}\rangle}{\langle R^2_{g,chain}\rangle} \qquad \rho = \frac{\sqrt{\langle R_g^2\rangle}}{\langle R_h\rangle}$$

Zimm, B. H.; Stockmayer, W. H. 1949 The Journal of Chemical Physics 17 1301

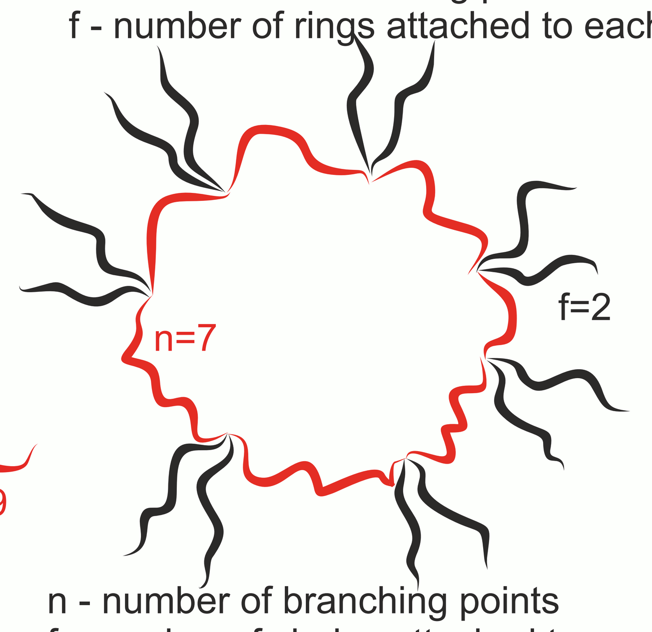
Hyperbranched polymers



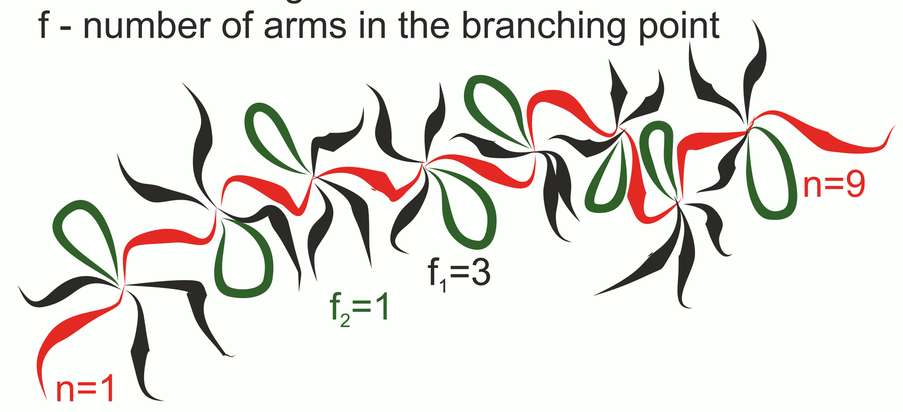
m - number of generations and
f - number of arms in the branching point



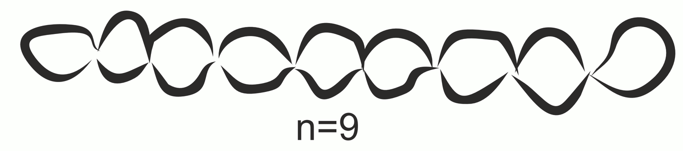
n - number of branching points
f - number of rings attached to each point



n - number of branching points
f - number of chains attached to each point



n - number of segments of the backbone
f_1 - number of chains attached to branching point
f_2 - number of rings attached to branching point



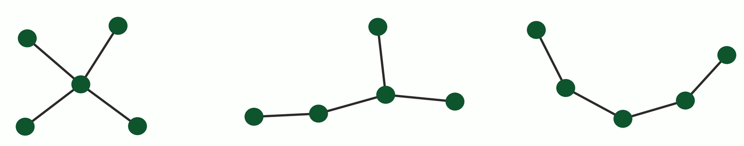
n=9
n - number of rings in the chain

Polymer nenworks

We consider graphs with fixed number of vertices N = 5 and variable parameter c (connectedness), defining the total number of links L=cN(N−1)/2 between vertices.

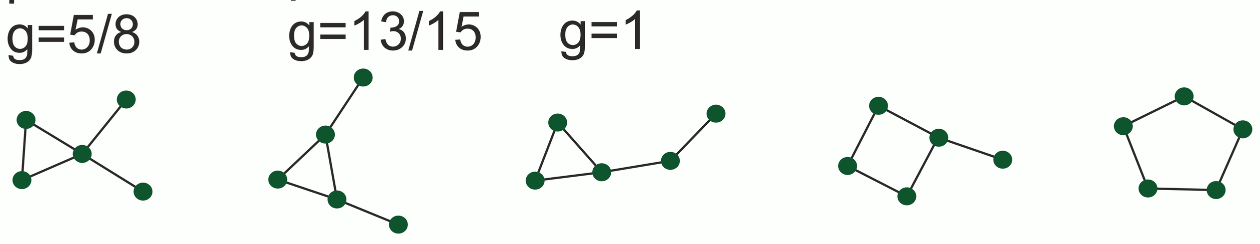
$0 \leqslant c \leqslant 1$

c=0.4



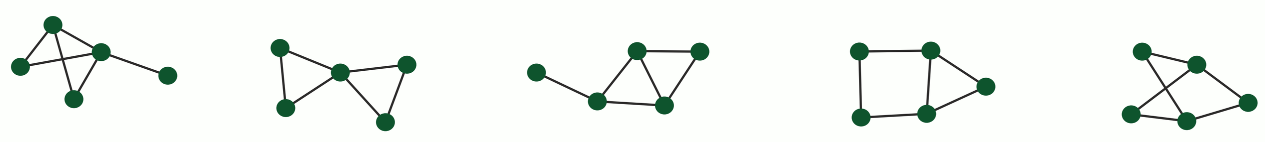
ρ=1.334 g=5/8 | ρ=1.423 g=13/15 | ρ=1.504 g=1

c=0.5



ρ=1.261 g=23/50 | ρ=1.282 g=123/250 | ρ=1.359 g=151/250 | ρ=1.262 g=61/125 | ρ=1.253 g=1/2

c=0.6



ρ=1.195 g=97/288 | ρ=1.217 g=3/8 | ρ=1.215 g=13/36 | ρ=1.189 g=139/396 | ρ=1.172 g=1/3

results for the ratio g are recalled from:

V. Blavatska, K. Haydukivska, Yu. Holovatch, 2020 J. Phys.: Condens. Matter 32 335102.

Results for the ratio ρ were also received exactly but unlike those for ratio g they cannot be expressed in terms of simple fractions thus we provide few first decimal numbers for their value.

Gyration radiuses for hyperbranched

Tree-like structure:

$$\langle R_g^2\rangle_{tree} = \frac{dL((f-1)^2)}{6(((f-1)^{m+1}-f+1)^2 f(f-2))}\Big(3(f-1)^{2m}(2f^2m-f^2-4fm-2f+2) +(f^2+2f-2)(4(f-1)^m-1)\Big)$$

Bottlebrush with rosettes:

$$\langle R_g^2\rangle_{bb} = \frac{dL}{12(f_1n+f_2n-f_1-f_2+n)^2}\Big(2f_1(3f_1+2)-8f_1(f_1+1)n+2(f_1+1)^2n^3 +f_2(2f_2-7)+7f_2n-2f_2(2f_2+1+f_1)n^2+2f_2(f_2+1+f_1)n^3\Big)$$

Rings decorated with rings:

$$\langle R_g^2\rangle_{rwr} = \frac{dL(n^2+(n^2+2n-1)f)}{12(f+1)n}$$

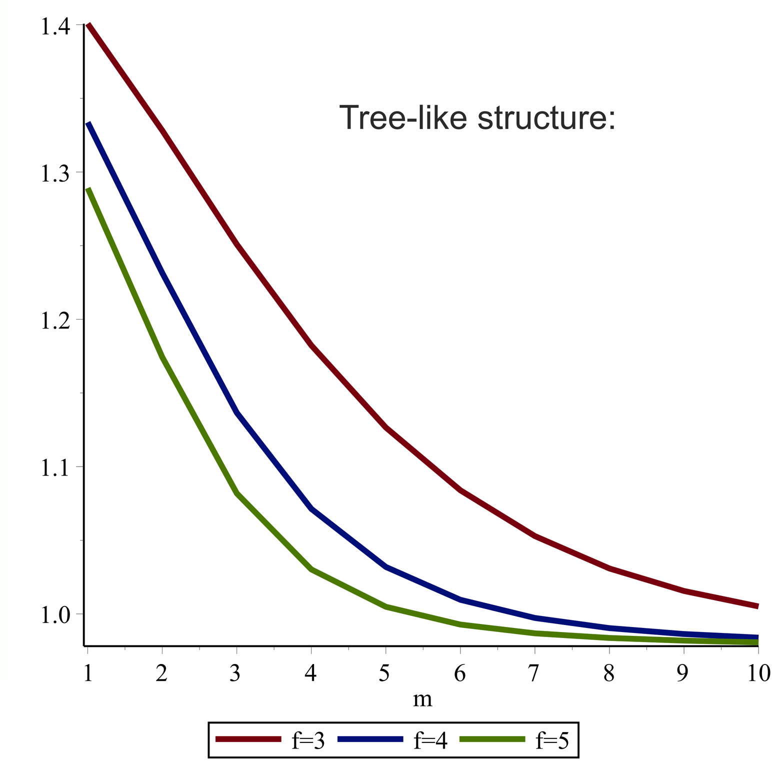
Rings decorated with stars:

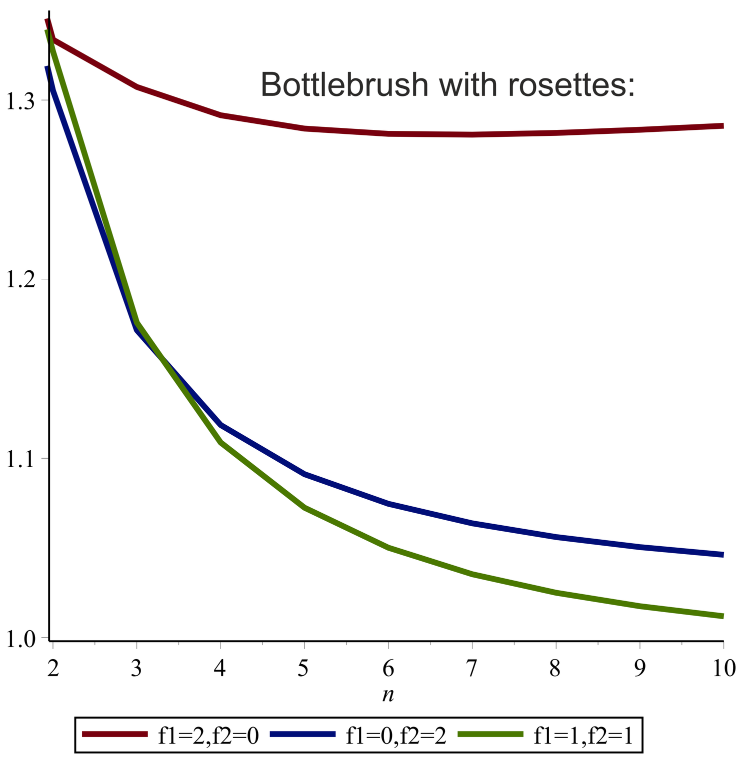
$$\langle R_g^2\rangle_{rws} = \frac{dL(6f(f+1)n+(f+1)^2n^2-f(f+4))}{12(f+1)^2n}$$

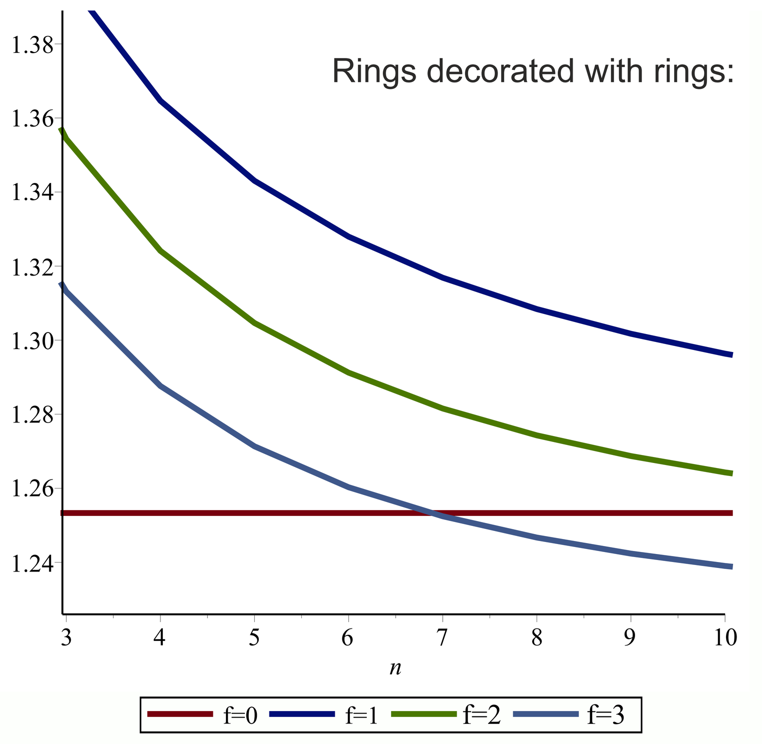
A row of rings:

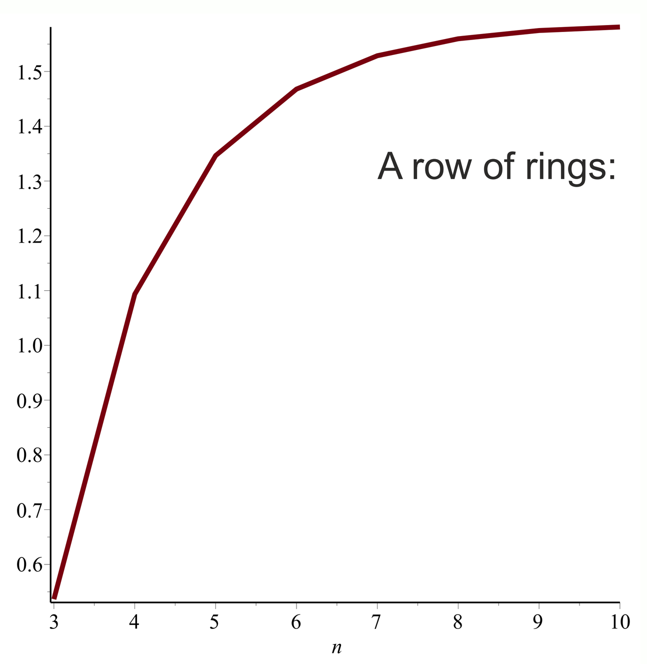
$$\langle R_g^2\rangle_{rr} = \frac{dL(n^3+7n^2-14n-12)}{24n^2}$$

Size ratio ρ for hyperbranched









Conclutions

Within the continuous chain model in its Gaussian approximation it is possible to calculate an exact values for the gyration radius and hydrodynamic radius for a number of hyperbranched structures. All of the considered structures are smaller in size then the chain of the same molecular mass, as is usualy the case for the branched polymers. For a number of the considered structures we observe a decrease of the ratio ρ with the increase of the branching parameter. How ever in case of a bottlebrush structure with only chains (f_2=0) and for a chain of rings we observe an increase of the ρ ratio with the increase of n, that in the limit of big n reaches the value typical for a simple chain.