Simple models for complex polymers: hyperbranched polymers

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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 $\theta$-point. Here we concentrate on polymers with multiple branching points that form periodic structures as well as some simple polymer networks.

Model and characteristics

$\sim$ Size characteristics

Gyration radius:

$\langle R_g^2 \rangle_{\text{hyperbranched}} = \frac{1}{12} \int d^2 \vec{r} \int d^2 \vec{r}' \frac{1}{N} \langle \rho(\vec{r}) - \rho(\vec{r}') \rangle^2$

Hydrodynamic radius:

$\langle R_h^2 \rangle_{\text{hyperbranched}} = \frac{1}{3} \int d^2 \vec{r} \int d^2 \vec{r}' \frac{1}{N} \langle \rho(\vec{r}) - \rho(\vec{r}') \rangle^2$

The averaging is performed with the partition function:

$Z_n(\beta) = \int d\rho \prod \theta(\rho(\vec{r}) - \rho(\vec{r}')) \exp \left( - \frac{N}{\beta} \int \frac{1}{2} \rho(\vec{r})^2 \right)$

where $\beta$ is an effective Hamiltonian of the $i$th strand: $H_i = \frac{N}{\beta} \left( \int d\rho \rho(\vec{r})^2 \right)$ and delta functions define the connection between them. Within the continuous chain model size characteristics are calculated using the identities:

$\langle \rho(\vec{r}) - \rho(\vec{r}') \rangle^2 = \frac{2}{\pi} \int \frac{d^2 \vec{k}}{d^2 \vec{k}'} \exp \left( - \frac{1}{\beta} \int \frac{1}{2} \rho(\vec{r})^2 \right)$

for the gyration radius and

$\langle \rho(\vec{r}) - \rho(\vec{r}') \rangle^2 = \frac{2}{\pi} \int \frac{d^2 \vec{k}}{d^2 \vec{k}'} \exp \left( - \frac{1}{\beta} \int \frac{1}{2} \rho(\vec{r})^2 \right)$

for the hydrodynamic radius.

Both characteristics are governed by the same scaling law ($R^2 \sim S^m$) with $S$ being the size of the chain.

$\sim$ Universal size ratio

$g = \frac{\langle R_g^2 \rangle_{\text{hyperbranched}}}{\langle R_h^2 \rangle_{\text{chain}}}$

$
\rho = \sqrt{\frac{\langle R_h^2 \rangle_{\text{hyperbranched}}}{\langle R_h^2 \rangle_{\text{chain}}}}$

$\rho \sim \rho_1^{(1)}$

$\rho \sim \rho_2^{(2)}$

$\rho \sim \rho_3^{(3)}$

$\rho \sim \rho_4^{(4)}$

$\rho \sim \rho_5^{(5)}$

Polymer networks

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.

$0 \leq c \leq 1$

$c = 0.4$

$p = 1.134$

$g = 5/8$

$c = 0.5$

$p = 1.261$

$g = 23/50$

$c = 0.6$

$p = 1.195$

$g = 97/288$

$c = 0.7$

$p = 1.29$

$g = 105/288$

Results for the ratio $g$ are recalled from:


Results for the ratio $p$ 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 radiiuses for hyperbranched

Tree-like structure:

$\langle R_g^2 \rangle_{\text{tree-like}} = \frac{dL(f-1)^2}{12(f^2-1)^m} \left( (f^2-1)^m - (f^2-1)^{m+1} \right)$

Bottlebrush with rosettes:

$\langle R_g^2 \rangle_{\text{bottlebrush with rosettes}} = \frac{dL}{12} \left( f^2 - 1 \right)^m \left( f^2 - 1 \right)^{-m+1}$

Rings decorated with rings:

$\langle R_g^2 \rangle_{\text{rings decorated with rings}} = \frac{dL(f+1)(f+2)}{12(f+1)^m}$

Conclusions
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 usually the case for the branched polymers. For a number of the considered structures we observe a decrease of the ratio $\rho$ with the increase of the branching parameter. How ever in case of a bottlebrush structure with only chains ($f = 0$) and for a chain of rings we observe an increase of the $\rho$ ratio with the increase of $n$, that in the limit of big $n$ reaches the value typical for a simple chain.