The shapes of ideal five junction comb polymers in two and three dimensions

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HIGHLIGHTS

- Mixed numeric and analytic methods are applied to determine polymer shape parameters.
- Semi-analytic and simulation results compare favorably.
- The method may easily be applied to other branched polymers structure.

ARTICLE INFO

ABSTRACT

This work investigates a variety of properties of eleven and fourteen branch five junction comb polymers in the ideal regime in two and three dimensions. A method based on the Kirchhoff matrix eigenvalue spectrum for arbitrary tree-branched polymers is used to compute shape properties and a scheme originally proposed by Benhamous (2004), is used to produce an exact equation for the form factor of the fourteen branch comb polymers. A Monte Carlo growth algorithm is also employed to compute the same properties. It is found that the values obtained by all of these methods are in fine agreement with each other and available theory.

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1. Introduction

In a set of previous papers [1–7] the shapes and the form factors of comb polymers containing two, three or four junctions have been computed by both analytical and Monte Carlo (MC) techniques. The agreement between these two approaches was excellent. Our sequence of investigations of multi-functional branch comb polymers provide a route to future studies of dendrimers [8] which contain concentric branched layers. These polymers have applications in drug delivery. In this note we extend our investigations to examine ideal five junction comb polymers with either eleven or fourteen branches (see Fig. 1). In these structures four of the branches are internal (joining junctions) and either seven or ten are external. If m is the number of monomers in a branch and b is the number of branches, there are a total of $N = b * m + 1$ units in these uniform combs.

An overall polymer size can be measured by the mean-square radius of gyration, $\langle S^2 \rangle$, where $\langle \rangle$ denotes an average over the polymer configurations. It is well-known [9] that for large polymers $\langle S^2 \rangle$ follows a scaling law. This result was originally

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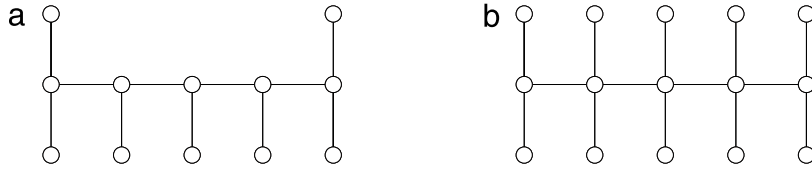
Fig. 1. Sketches of the 11 and 14 branched comb polymers discussed in this paper in *a* and *b* respectively.

obtained for the number of bonds, $N - 1$, but as $N \to \infty$ the distinction between the number of bonds and the number of units vanishes. The scaling law is

$$\langle S^2 \rangle = CN^{2\nu}. \tag{1}$$

The coefficient, C, is a model dependent amplitude but the exponent, 2ν, is universal and equal to 1 for all ideal polymers of any topology. However, in our Monte Carlo calculations we have employed the $N - 1$ factor for finite systems.

The compactness of a given polymeric structure is measured by the g-ratio, involving the respective radii of gyration of a branched, $\langle S^2 \rangle_b$, and a linear structure, $\langle S^2 \rangle_l$, containing the identical number of units. Casassa and Berry [10] obtained a general equation for the g-ratio of uniform, ideal comb polymers in any dimension which have n three-functional junctions regularly spaced along the backbone:

$$g = \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_\ell} = r - \frac{r^2(1-r)}{(n+1)} + \frac{2r(1-r)^2}{n} + \frac{(3n-2)(1-r)^3}{n^2}. \tag{2}$$

Here, r is the ratio of the number of units in the comb backbone to the total number of units in the polymer. In the case of the 11 branch combs, $r = 6/11$ and $n = 5$, so $g = 821/1331$ (0.61683). The g-ratio of ideal 14 branch polymers is determined from a calculation of the form factor [3] derived later in this article. Its value is 163/343 (0.47522).

Details about the shapes of polymers can be determined from the radius of gyration tensor. Its eigenvalues, ordered by magnitude are $e_1 \le e_2$ in two dimensions and $e_1 \le e_2 \le e_3$ in three. These are the principal moments of gyration along the principal orthogonal axes [11]. The average trace of this tensor, $e_1 + e_2$ or $e_1 + e_2 + e_3$, is equal to $\langle S^2 \rangle$. Rudnick and Gaspari [12,13] have defined the average asphericity, $\langle A \rangle$, of polymers in d dimensions as

$$\langle A \rangle = \left\langle \frac{\sum\limits_{i>j}^{d}(e_i - e_j)^2}{(d-1)\left(\sum\limits_{i=1}^{d} e_i\right)^2} \right\rangle. \tag{3}$$

The shape of a three (two) dimensional linear polymer can vary from a fully extended rod in which only e_1 does not vanish so that $\langle A \rangle$ has unit value, to a sphere (circle) for which all the e s are equal. In the latter case $\langle A \rangle$ is zero. In between the extremes of a rod and a sphere (circle), a polymer configuration can be imagined as approximately enclosed inside an ellipsoid (ellipse).

There are other indicators of the shape; in two dimensions $\langle \delta_1 \rangle$ and in three dimensions $\langle P \rangle$. These are defined as

$$\langle \delta_1 \rangle = \frac{\langle e_1 \rangle}{\langle S^2 \rangle}, \tag{4}$$

and

$$\langle P \rangle = \left\langle \frac{27(e_1 - \bar{e})(e_2 - \bar{e})(e_3 - \bar{e})}{\left(\sum\limits_{i=1}^{3} e_i\right)^3} \right\rangle \tag{5}$$

respectively. Here, $\bar{e}$ is

$$\bar{e} = \frac{e_1 + e_2 + e_3}{3}. \tag{6}$$

Note that $\langle A \rangle$ and $\langle P \rangle$ involve an average of a ratio whereas $\langle \delta_1 \rangle$ involves a ratio of averages.

Another important structural property of polymers is the form factor, $S(k)$, which provides information about the spatial monomer distribution. It is defined [14] as the Fourier transform of the density–density autocorrelation function:

$$S(k) = \frac{1}{N^2} \sum\limits_{m,n}^{N} \langle e^{i\mathbf{k} \bullet (\mathbf{R}_n - \mathbf{R}_m)} \rangle \tag{7}$$

where $\mathbf{k}$ is the momentum transfer of the scattering experiment and $\mathbf{R}_m$ and $\mathbf{R}_n$ are the positions of the mth and nth monomers.