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The two dimensional shapes of simple three and four junction ideal comb polymers

Robin de Regt [a], Marvin Bishop [b], Adam J. Barillas [b], Tylor Borgeson [b], Christian von Ferber [a,*]

[a] Coventry University, Coventry, UK

[b] Manhattan College, Manhattan, NY, United States

HIGHLIGHTS

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

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ABSTRACT

We redesign and apply a scheme originally proposed by Wei (1995) [2,3] to produce numerical shape parameters with high precision for arbitrary tree-branched polymers based on their Kirchhoff matrix eigenvalue spectrum. This algorithm and a Monte Carlo growth method on square and triangular lattices are employed to investigate the shapes of ideal three and four junction two dimensional comb polymers. We find that the extrapolated values obtained by all of these methods are in excellent agreement with each other and the available theory. We confirm that polymers with a complete set of interior branches display a more circular shape.

1. Introduction

In a previous publication von Ferber et al. [1] investigated the shapes of three and four junction comb polymers by redesigning a scheme originally proposed by G. Wei [2,3] to produce numerical shape parameters of arbitrary tree-branched polymers based on the Kirchhoff matrix eigenvalue spectrum. The predictions of this method and the simulation results of two different Monte Carlo (MC) techniques (pivot and growth) were compared for 5, 7, 8, 9 and 11 branch combs. See Fig. 1 which illustrates the connectivity of the branches. In all of these uniform comb structures, if m is the number of monomers (“beads”) in a branch and b is the number of branches, there are a total of $N = bm+1$ units. It was found that the extrapolated property values obtained by all the methods were in excellent agreement with each other and the available theory in the ideal regime. This paper further tests the redesigned scheme by examining corresponding two dimensional systems.

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 [4] that for large polymers, with or without branches, $\langle S^2 \rangle$ follows a

* Corresponding author.
E-mail addresses: deregtr@uni.coventry.ac.uk (R. de Regt), marvin.bishop@manhattan.edu (M. Bishop), abarillas.student@manhattan.edu (A.J. Barillas), tborgeson.student@manhattan.edu (T. Borgeson), c.vonferber@coventry.ac.uk (C. von Ferber).

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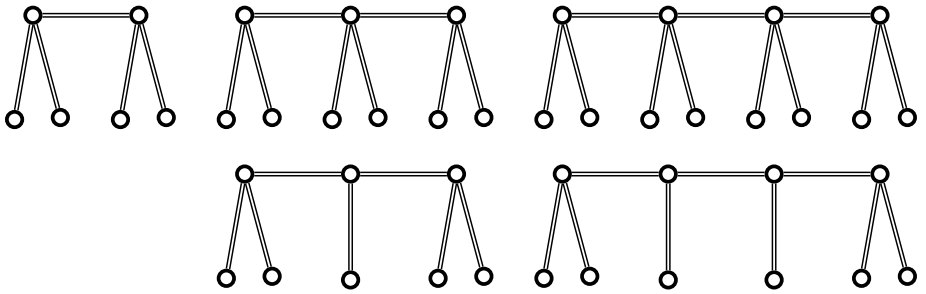

Fig. 1. Sketches of the 5, 7, 8, 9, and 11 branched comb polymers discussed in this paper.

scaling law:

$$\langle S^2\rangle = C(N-1)^{2\nu}. \tag{1}$$

The coefficient, C, is a model dependent amplitude but the exponent, 2ν, is universal and equal to 1.0 for all ideal polymers in two dimensions.

If $\langle S^2\rangle_b$ and $\langle S^2\rangle_l$ are the mean-square radii of gyration of a branched and linear structure with an identical number of monomers, then the g-ratio, a useful parameter for comparing the compactness of linear and branched polymers, is defined as

$$g = \frac{\langle S^2\rangle_b}{\langle S^2\rangle_l}. \tag{2}$$

Casassa and Berry [5] obtained a general equation for the g-ratio of uniform, ideal comb polymers with f three-functional junctions regularly spaced along the backbone:

$$g = 1 - r - \frac{r^2(1-r)}{(f+1)} + \frac{2r(1-r)^2}{f} + \frac{(3f-2)(1-r)^3}{f^2}. \tag{3}$$

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 five branch combs, $r = 3/5$ and $f = 2$, so $g = 89/125(0.7120)$. In the seven branch case $r = 4/7, f = 3$ and $g = 229/343(0.6676)$ whereas for nine branches $r = 5/9, f = 4$ and $g = 155/243(0.6379)$. The g-ratios of ideal eight and eleven branch polymers were determined by von Ferber et al. [6] from the form factor. These values are 37/64 (0.5781) and 683/1331 (0.5131) for eight and eleven branches, respectively. Note that all of these results are independent of the spatial dimension.

The shape of any polymer composed of N units can be determined from the matrix representation of the radius of gyration tensor, $\overleftrightarrow{T}$. If X_j^α denotes the α component of the two dimensional position vector of the jth polymer bead, then the center of mass coordinates, $X_{CM}^{(\alpha)}$, of a given configuration are given by

$$X_{CM}^{(\alpha)} = \frac{1}{N}\sum_{j=1}^{N} X_j^{(\alpha)}, \quad \text{where } \alpha = 1 \text{ or } 2 \tag{4}$$

and the matrix components of $\overleftrightarrow{T}$ may be written in the form

$$T_{\alpha\beta} = \frac{1}{N}\sum_{j=1}^{N}(X_j^{(\alpha)} - X_{CM}^{(\alpha)})(X_j^{(\beta)} - X_{CM}^{(\beta)}). \tag{5}$$

This tensor has eigenvalues e_1 and e_2, which are the principal moments of gyration along the principal orthogonal axes [7]. The average trace of this tensor, $e_1 + e_2$, is equal to $\langle S^2\rangle$. The eigenvalues of each configuration are ordered by magnitude, $e_1 \geq e_2$. Rudnick and Gaspari [8,9] have defined the average asphericity, $\langle A\rangle$, of polymers in two dimensions as

$$\langle A\rangle = \left\langle \frac{(e_1 - e_2)^2}{(e_1 + e_2)^2} \right\rangle. \tag{6}$$

These averages are over all sets of eigenvalues determined from the simulated configuration. Note that in these equations $\langle A\rangle$ involves the average of a ratio and not the ratio of an average.

The shape of a two dimensional linear polymer can vary from a fully extended rod in which e_2 essentially vanishes so that $\langle A\rangle$ has unit value, to a circle for which $e_2 = e_1$. In the latter case $\langle A\rangle$ is zero. More complex polymer structures such as those studied here can obtain a fully extended rod shape in the ideal regime because the units can overlap each other.