MONTE CARLO STUDIES OF IDEAL MULTI-BRANCHED POLYMERS

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Abstract

Many polymer properties are altered by branching. Monte Carlo computer simulation is a useful tool for exploring these changes. This paper examines one, two, and three-junction ideal polymers. The current simulations are in fine agreement with theoretical and other simulation studies. This area of polymer science provides a store of possible student projects. In order to work in this field, students need to master both computer programming and statistics.

Introduction

It is well-known that the presence of branching alters the behavior of polymeric materials. Since highly branched structures are of current interest in applications such as nano-cages for drug delivery, it is important to systematically investigate the influence of increased branching. There have been many studies of the properties of star polymers. These contain a central junction point with f branches of equal length connected to it. A three-branched star is represented in Figure 1 by B whereas a non-branched linear chain is represented by A. The simplest two-junction polymers are H-comb polymers. These polymers have a central "backbone" branch connecting the two junctions together and each of these junctions also has two other branches attached to them. Thus, H-comb polymers contain one internal branch and four external branches for a total of five branches. These are represented by C in Figure 1. One can imagine an H-comb as a three branched star with two extra branches attached to the end of any of the three branches. The simplest three-junction polymers are the TTT and HH-comb polymers which contain seven and eight branches, respectively. These are represented by D and E in Figure 1. In TTT-combs two branches are internal (e.g. connect junctions) and five are external, whereas in HH-combs there are two internal and six external branches. A TTT polymer can be envisioned as an H-comb with two additional branches attached to the end of one of its external branches. Finally, the HH-comb is formed by

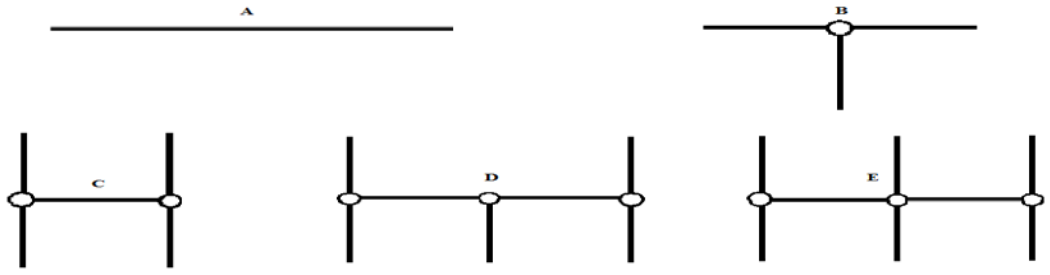

Figure 1: Two dimensional projections of the different polymers: (A) Linear, (B) 3-Branched Star, (C) H-comb, (D) TTT-comb, and (E) HH-comb.

attaching the end of one branch of a three-branch star to a junction of another 3-branched star, and then attaching two further branches.

In a previous publication in this journal, Zajac and Bishop [1] used a Monte Carlo growth method to simulate three dimensional ideal linear polymers. They computed a variety of polymer properties such as the mean-square radius of gyration, $<S^2>$, its components along the principal orthogonal axes [2], λ_1, λ_2, and λ_3, and the mean asphericity, <A>. They found excellent agreement with theoretical values. In this work, the same Monte Carlo growth method is extended to simulate ideal three, five, seven, and eight-branched polymers in three dimensions.

Method

Each growth algorithm utilizes the linear polymer growth algorithm as described in Zajac and Bishop [1], with slight modifications. In the case of the three-branched star, the first polymer unit is placed at the origin (0, 0, 0). The first branch is grown to include a pre-specified number of polymer units, N. Then, the second branch is started once again at the origin, and grown to include N additional units. The same method is employed for the third branch. Note that this growth technique places three overlapping units at the origin. In the case of the H-comb, a three-branched star is grown as described above. However, this time, a new origin is moved to the end of the third branch of the star and then two more branches are grown from this new origin. For the TTT-comb, first an H-comb is grown. Then, a new origin is moved to the end of the fifth branch, where two more branches are grown. Finally, for the HH-comb, one three-branched star is grown from the end of another. Then, two more branches are grown from the end branch of the second star. After each polymer is completely constructed, a number of properties are calculated for that configuration, as was done in Zajac and Bishop [1]. One additional property examined here is the g-ratio, which is the ratio of the radii of gyration of a branched polymer to a linear one when both polymers contain the same number of units. The radii of gyration of all polymers are known to follow the scaling law [3]

$$<S^2> = C\,(TN - 1)^{2\nu} . \qquad (1)$$

Here, TN is the total number of units (TN = f * N). The coefficient, C, is a model dependent amplitude but the exponent, 2ν, is universal and equal to 1.00 for all large ideal polymers. The g-ratio for ideal f-branch star polymers has been obtained by Zimm and Stockmayer [4]:

$$g_{star} = (3f - 2) / f^2 . \qquad (2)$$

Hence, when f = 3, g_{star} = 0.778. Casassa and Berry [5] obtained a general equation for the g-ratio of uniform, ideal comb polymers with j three-functional junctions regularly spaced along the backbone:

$$g_{comb} = r - r^2 (1 - r) / (j + 1) + 2\, r\, (1 - r)^2 / j + (3j - 2)\, (1 - r)^3 / j^2 . \qquad (3)$$

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 H-combs, r = 3/5 and j = 2, thus g_{comb} = 0.712. TTT-combs have r = 4/7 and j = 3, giving g_{comb} = 0.668. Von Ferber, *et al* [6] found the g-ratio of HH-combs, 0.578, by examining the form factor.

Results

The simulation has been developed using the Visual Studio C++ compiler on a PC. All the runs employed 10,000 independent samples and the results are contained in Tables I and II. The errors have been calculated via the methods of Zajac and Bishop [1]. In the tables the number in parenthesis denotes one standard deviation in the last displayed digit; for example, $<\lambda_1>$ = 5.08(2) means that $<\lambda_1>$ = 5.08 ± 0.02.

Table I: Properties of Multi-Branched Polymers as a Function of the Number of Units per Branch, N.

N	$\langle\lambda_1\rangle$	$\langle\lambda_2\rangle$	$\langle\lambda_3\rangle$	$\langle S^2\rangle$	$\langle A\rangle$	$\langle\lambda_1\rangle/\langle S^2\rangle$	$\langle\lambda_2\rangle/\langle S^2\rangle$	$\langle\lambda_3\rangle/\langle S^2\rangle$
3-Branched								
20	5.08(2)	1.74(1)	0.625(3)	7.44(3)	0.294(1)	0.682(1)	0.234(1)	0.084(1)
30	7.76(4)	2.61(1)	0.940(4)	11.32(4)	0.299(1)	0.686(1)	0.231(1)	0.083(1)
40	10.48(5)	3.52(2)	1.26(1)	15.26(6)	0.301(1)	0.687(1)	0.231(1)	0.082(1)
50	13.15(6)	4.43(2)	1.58(1)	19.15(8)	0.300(1)	0.686(1)	0.231(1)	0.082(1)
60	15.80(8)	5.29(3)	1.89(1)	22.97(9)	0.301(1)	0.688(1)	0.230(1)	0.082(1)
5-Branched								
20	7.84(4)	2.48(1)	1.01(1)	11.34(5)	0.294(2)	0.692(1)	0.219(1)	0.089(1)
30	11.90(6)	3.77(2)	1.55(1)	17.22(7)	0.293(2)	0.691(1)	0.219(1)	0.090(1)
40	16.10(9)	5.07(2)	2.05(1)	23.22(10)	0.296(2)	0.693(1)	0.218(1)	0.088(1)
50	20.06(11)	6.39(3)	2.59(1)	29.04(12)	0.294(2)	0.691(1)	0.220(1)	0.089(1)
60	24.43(13)	7.67(3)	3.10(1)	35.20(15)	0.297(2)	0.694(1)	0.218(1)	0.088(1)
7-Branched								
20	10.27(6)	3.18(1)	1.37(1)	14.82(6)	0.292(2)	0.693(1)	0.215(1)	0.092(1)
30	15.57(9)	4.88(2)	2.08(1)	22.53(9)	0.289(2)	0.691(1)	0.217(1)	0.092(1)
40	21.12(12)	6.53(3)	2.77(1)	30.42(13)	0.295(2)	0.694(1)	0.215(1)	0.091(1)
50	26.59(15)	8.21(3)	3.47(1)	38.28(16)	0.295(2)	0.695(1)	0.214(1)	0.091(1)
60	31.98(18)	9.90(4)	4.18(2)	46.06(19)	0.294(2)	0.694(1)	0.215(1)	0.091(1)
8-Branched								
20	9.78(5)	3.41(1)	1.51(1)	14.70(6)	0.258(1)	0.665(1)	0.232(1)	0.103(1)
30	14.94(8)	5.18(2)	2.29(1)	22.41(8)	0.259(1)	0.667(1)	0.231(1)	0.102(1)
40	19.86(10)	6.94(3)	3.06(1)	29.86(11)	0.257(1)	0.665(1)	0.232(1)	0.103(1)
50	25.26(13)	8.78(4)	3.85(1)	37.89(15)	0.260(1)	0.667(1)	0.232(1)	0.102(1)
60	30.35(16)	10.55(4)	4.63(2)	45.53(18)	0.260(1)	0.667(1)	0.232(1)	0.102(1)

Table II: Radii of Gyration of Linear Polymers.

N	$\langle S^2\rangle$	N	$\langle S^2\rangle$
60	10.01(5)	240	40.00(20)
90	14.96(7)	250	41.69(21)
100	16.81(9)	280	46.82(24)
120	19.91(10)	300	50.26(26)
140	23.45(12)	320	53.36(27)
150	25.03(13)	350	58.54(30)
160	26.77(14)	400	67.02(34)
180	29.98(15)	420	70.34(36)
200	33.60(17)	480	80.56(42)
210	35.01(18)		

The $\langle S^2\rangle$ data in Tables I and II were fit by a weighted nonlinear least-squares program [7] to determine the exponent in the scaling laws, Eq.1, and the results are listed in Table III. These results are consistent with the theoretical value of 1.00.

Table III: Scaling Exponent.

Type	2ν
Linear	0.996(2)
3-Branches	1.02(1)
5-Branches	1.02(1)
7-Branches	1.03(1)
8-Branches	1.03(1)

The computer results in the Tables are for a finite TN, whereas the theoretical results are for an infinite number. Another scaling law for any property P is

$$P = P_\infty (1 - K / TN^\Delta) \quad . \qquad (4)$$

Here P_∞ is the value of P for infinite TN, K is a constant, and Δ is the finite scaling exponent. In the ideal polymer regime, Δ has a value of 1.00. The P_∞ value can thus be found by fitting a weighted least-squares line [7] in 1/TN to each set of data in the Tables. Then the best linear fit was extrapolated in 1/TN to 0 (e.g. TN → ∞). The final extrapolated values are presented in Table IV along with known theoretical and simulation results. All of the current simulation values reported in Table IV are well within two standard deviations of the mean, or in the 95% confidence interval.

The ratios of the eigenvalues, $\langle\lambda_1\rangle/\langle\lambda_3\rangle$ and $\langle\lambda_2\rangle/\langle\lambda_3\rangle$, were computed from the data in Table IV and the results are presented in Table V.

Table V: Ratios of Eigenvalues, $\langle\lambda_1\rangle/\langle\lambda_3\rangle$ and $\langle\lambda_2\rangle/\langle\lambda_3\rangle$.

Type	$\langle\lambda_1\rangle/\langle\lambda_3\rangle$	$\langle\lambda_2\rangle/\langle\lambda_3\rangle$
3-Branches	8.52	2.81
5-Branches	7.79	2.46
7-Branches	7.72	2.38
8-Branches	6.55	2.27

Solc [11] also simulated ideal 3-branched stars in three dimensions. He found ratios of 8.47 and 2.83. The current simulation values are in good agreement with his results. These ratios, as well as the mean asphericity values, <A>, indicate that increased branching makes the polymers more symmetrical.

Conclusion

We have investigated multi-branched, three dimensional ideal polymers using Monte Carlo growth methods. Many different properties have been computed. There is fine agreement with theoretical results and other simulations. Modeling projects such as the one described here provide a clear demonstration of some aspects of polymers and thus strongly enhance student understanding and intuition.

Appendix: The Manhattan College Undergraduate Research Program

Manhattan College has a long tradition of involving undergraduates in research and was one of the original members of the Oberlin 50.

Table IV: Comparison of Computer Simulation and Literature Results.

	3 Branches		5 Branches		7 Branches		8 Branches	
Property	Computer	Literature	Computer	Literature	Computer	Literature	Computer	Literature
<A>	0.305(1)	0.304(a)	0.297(2)	0.297(d)	0.296(2)	0.295(d)	0.260(1)	0.261(d)
g-ratio	0.780(6)	0.778(b)	0.711(5)	0.712(e)	0.668(5)	0.668(e)	0.574(4)	0.578(f)
$\langle\lambda_1\rangle/\langle S^2\rangle$	0.690(1)	0.691(c)	0.693(1)		0.695(1)		0.668(1)	
$\langle\lambda_2\rangle/\langle S^2\rangle$	0.228(1)	0.228(c)	0.219(1)		0.214(1)		0.232(1)	
$\langle\lambda_3\rangle/\langle S^2\rangle$	0.081(1)	0.081(c)	0.089(1)		0.090(1)		0.102(1)	

(a) reference 8 (b) reference 4 (c) reference 9 (d) reference 10 (e) reference 5 (f) reference 6.

This is a group of undergraduate institutions whose students have produced many PhDs in engineering and science. At Manhattan College, students can elect to take an independent study course for three credits during the academic year. In addition, the College provides grant support to the students for ten weeks of work during the summer. I have personally recruited the students from my junior level course in Systems Programming. Previously published articles in this journal by Manhattan College student co-authors are a very effective recruitment tool. The students have also presented their results at a variety of undergraduate research conferences including the Hudson River Undergraduate Mathematics Conference and the Spuyten Duyvil Undergraduate Mathematics Conference.

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