

Structural properties and scaling of the radius of gyration of two-dimensional star-branched polymers grown by diffusion

Guillermo Ramírez-Santiago^{a,*}, Carlos I. Mendoza^b

^a*Departamento de Física-Química, Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, 01000 México, D.F., Mexico*

^b*Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, 04510 México, D.F., Mexico*

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Abstract

We built up star-branched polymers, whose morphology is fully determined by diffusion, with $p = 1, 3, 6$ and 12 branches with a total of 30,000 monomer units. We investigated their structural properties by calculating the monomer–monomer correlation functions. A detailed finite size scaling analysis of the radius of gyration was also performed to determine the exponent and the corrections to scaling. From these results we calculated the fractal dimension of the branched aggregates and obtained: $d_f = 1.222(7)$, for the linear chain, $d_f = 1.2305(8)$, $d_f = 1.247(8)$ and $d_f = 1.261(8)$ for the three, six and twelve branches polymer, respectively.

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1. Introduction

Star-branched polymers are materials with many fascinating properties. They play an important role in different chemical and physical polymerization processes. Due to their well-defined molecular architecture these systems can be regarded as models with soft and ultra-soft inter-particle interactions. Because they interpolate in between hard colloids with strong repulsive core on one side, and as soft and flexible polymeric systems, on the other, they are relevant as soft condensed matter systems. Since the prediction and interpretation of the conformational properties of branched polymers is difficult, numerical simulations are very useful to shed some light on the structural and conformational properties of these branched systems.

A number of algorithms based upon on-lattice diffusion [1,2] or kinetic processes [3,4] have been developed to describe the irreversible growth of linear polymers. Some of them have the property of producing polymers that grow indefinitely [4] without forming cages. In this paper we introduce an off-lattice algorithm based

*Corresponding author. Tel.: + 52 5622 5081; fax: + 52 5622 5015.

E-mail address: memo@fisica.unam.mx (G. Ramírez-Santiago).

upon a pure diffusive process to construct branched polymers. This algorithm allows conformations in which one or more branches may end up confined (trapped), in which case the process terminates. Nonetheless, due to the directed processes used to grow the branched structures, the algorithm is less sensitive to attrition than a self-avoiding walker. We have built up two-dimensional star-branched polymers with one, three, six and twelve branches. An statistical analysis of the structural and conformational properties of these structures over an ensemble with one hundred different configurations yielded fractal dimension values that appear to increase slightly as the number of branches increases.

2. The algorithm

In this section we introduce the off-lattice algorithm to construct a diffusion-limited star-branched polymer (DLSP) in two dimensions. To built up the structures we consider monomers that are bi-functional. To begin with the construction process one first defines the branching topology of the desired DLSP, that is, one defines the number of arms or branches that the star polymer will have. For instance, in Fig. 1 we show the topology of a DLSP with three branches. In such a case the monomers are numbered in a convenient way so that a given monomer is linked to a *target* monomer. In the scheme shown in Fig. 1, monomers 2, 3, and 4 are linked to monomer number 1. Monomer number 5 is linked to monomer 2, monomer 6 is linked to monomer 3, and so on and so forth. In this way each of the N monomers of the structure is linked to a specific *target* monomer. Once the topology is defined and the monomers are numbered, the building process starts with a *seed* monomer of diameter d —labeled as number 1—located at the origin. Then, a second monomer is released from an arbitrary point on a circle of radius R_0 centered at the *seed* monomer. This second monomer performs a random walk until it reaches the corresponding *target* monomer within a distance d —distance center to center—in which case it attaches to it at the contact point. If it becomes far away from the *target* monomer then it is deleted and a new monomer is released. The process iterates until the aggregate reaches its final mass. The described procedure is sketched in Fig. 2. The radius R_0 is chosen from a uniform random distribution such that its value is in between the monomer's radius $a = d/2$ and the radius of the smallest circle that encloses completely the structure already grown. To speed up the simulation we used a step size control based on a recursive procedure that allows a rapid approach of the incoming monomer to the aggregate without hindering large excursions [5].

3. Results

3.1. Structural properties

In Fig. 3, panels (a)–(d), we show typical star branched polymer configurations with, $p = 1, 3, 6,$ and 12 branches, with up to $N = 30,000$ monomer units. They were obtained by applying the algorithm described in

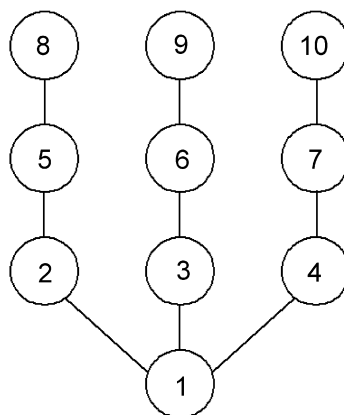


Fig. 1. Schematic sketch of the topology of a three-arm star polymer.

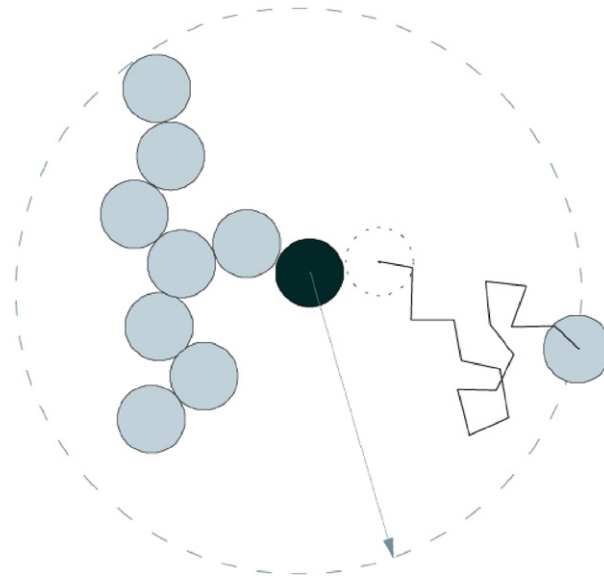


Fig. 2. Sketch that shows the procedure to built a DLSP. The black disc represents the *target* monomer.

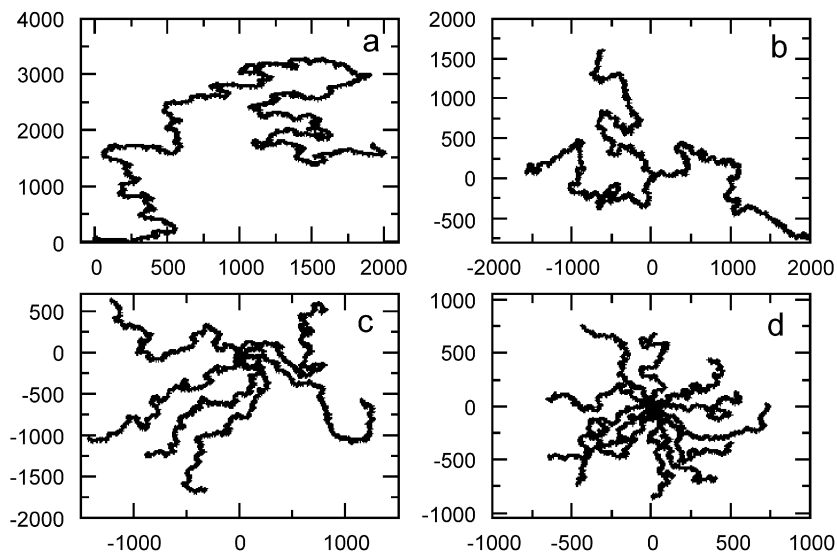


Fig. 3. Representative DLSP configurations. (a) Single-branch polymer, (b) three-branch star polymer, (c) six-branch star polymer and (d) twelve-branch star polymer.

Section 2. Note that the wiggles present in the arms are mainly due to the diffusive process used to build the structures. To understand the structural properties and estimate the compactness of the structures we calculated the monomer–monomer correlation functions, $g(r)$. From these correlations we estimated the fractal dimension of each branched-polymer since at intermediate distances, $g(r) \sim r^{d_f-2}$ with d_f the fractal dimension. The monomer–monomer correlation functions were calculated by means of the usual histogram method [6]. For the sake of clarity we describe briefly this method: A monomer is chosen at random and the distances r to all other monomers are calculated from this reference particle. The histogram of the distance distribution, $N(r, \Delta)$ is obtained by counting the number of distances that fall in the interval $(r, r + \Delta)$. The monomer–monomer correlation function, $g(r)$, of the two-dimensional branched structures is then calculated

by means of the formula, $g(r) = N(r, r + \Delta)/(2\pi r\Delta)$. After all the monomers of the structure have been swept, an average of the histograms is carried out.

We applied this method to calculate $g(r)$ to structures with one, three and six arms. An average of this quantity over an ensemble of 100 different configurations was carried out for each branched structure. In Fig. 4 we show the results for the monomer–monomer correlation functions for DLSP with one, three, six and twelve arms. One sees that at small distances, up to $r/a \approx 10$, the curves fall on top of each other. In addition, one can see for distances up to $r/a \approx 4$, a three peak structure at integer multiples of the excluded volume diameter. This structure is reminiscent of that observed in simple liquids and it has also been obtained in the case of homopolymer rings in a poor solvent [7]. At larger distances, $r/a > 10$, the curves for star polymer structures with more than one arm depart from that corresponding to a single arm. This departure from the single arm polymer becomes more important as the number of branches increases. This increase in monomer–monomer correlations is related to an increase in monomer density at relatively large distances due to the branched structure. One also observes that the correlations for the branched structures fall off to zero more rapidly—at smaller distances—as the number of arms increases. This happens because of the finiteness of the systems, that is, for a fixed total number of monomers N in the branched structure, an increase in the number of arms leads to shorter branches.

As mentioned above, we are mainly interested in the existence of a power law behavior of the monomer–monomer correlations at intermediate distances, that is, $g(r) \sim r^{d_f-2}$, with d_f the fractal dimension of the structure. Thus, we plotted $g(r)$ versus r on a log–log scale to identify the power law behavior and get an estimate of d_f . Representative results of this analysis are shown in Fig. 5, panels (a)–(d), where we plotted the average of the correlation functions over an ensemble of one hundred statistically independent structures. Each structure has a total of $N = 30,000$ monomers and $p = 1, 3, 6,$ and 12 branches, respectively. In this way we obtained the following fractal dimension values: $d_f = 1.22(1)$, $d_f = 1.23(3)$, $d_f = 1.24(2)$, and $d_f = 1.26(3)$, for $p = 1, 3, 6,$ and 12 arms, respectively. The digits in parenthesis indicate the size of the error bar, it has to be added or subtracted to the last significant figure of the fractal dimension. These results suggest that the polymer structure becomes more compact as the number of branches increases. Nonetheless, the error bars are not small enough to be able to make a definite conclusion. To try to obtain a more precise estimate of d_f in subsection 3.2 we will carry out a detailed finite size scaling analysis of the radius of gyration.

One should also note that not only the fractal dimension of the structures appear to increase with the number of branches, but also, for the star with 12 arms a second linear region in $g(r)$ shows up. This second linear region is rather related to the average density profile and not to the fractal dimension of the structure [8]. For stars with a large number of branches this second linear region should appear more clearly. On the other hand, one should also note that the values of the fractal dimensions obtained here for the DLSP branched structures are slightly smaller than the corresponding thermodynamically equilibrated counterparts. That is, if

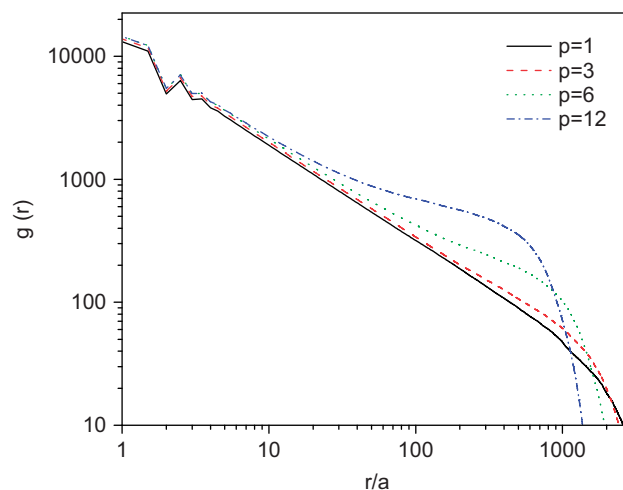


Fig. 4. Monomer–monomer correlation functions as a function of distance for different star branching polymers.

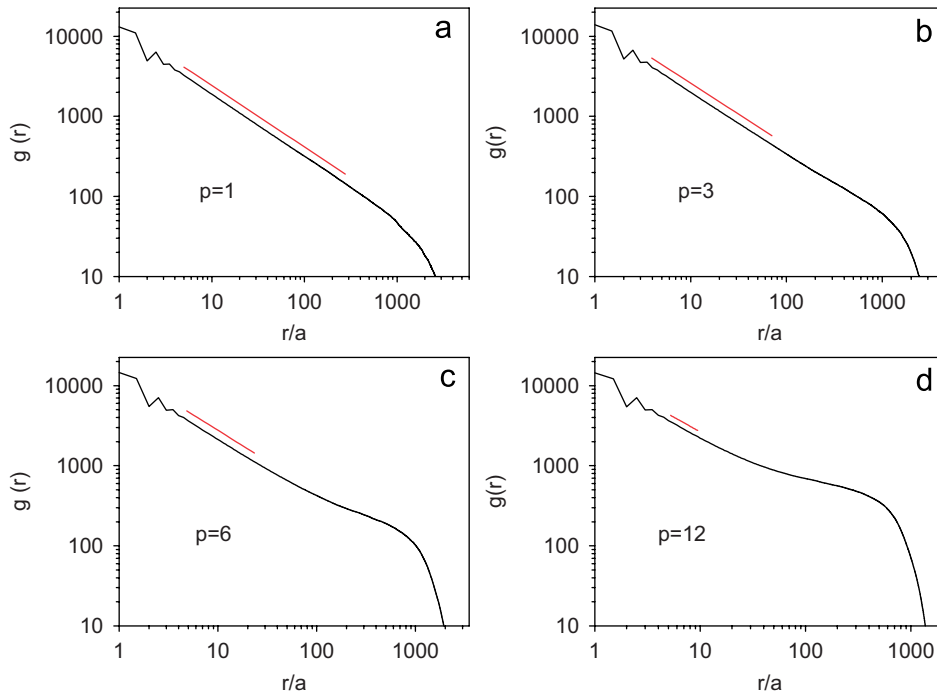


Fig. 5. Here we show the linear part of the monomer–monomer correlation functions that was considered for the evaluation of the fractal dimension of the DLSP (a) single-arm polymer, (b) three-arm polymer, (c) six-arm polymer and (d) twelve-arm polymer.

we were to consider polymers with the same branched structure, but those in which the monomers can move freely but maintaining the connectivity, and avoiding overlapping, the fractal dimensions that we would obtain should be slightly larger than the ones we obtained in the present analysis. For instance, in the case of a two-dimensional self-avoiding walk linear polymer, the fractal dimension of the fully equilibrated structure is 1.33. This value is higher than the estimated value 1.23, obtained for the equivalent diffusively built linear structure of the present paper. On the other hand, one should also consider the ability of the present algorithm to simulate branched structures with up to $N = 30,000$ monomer units or even larger systems at the expense of an increase in computing time.

3.2. Conformational properties

To analyze the conformational properties of the DLSP branched structures build up here we also carried out a detailed finite size scaling analysis of the average of the radius of gyration, $\langle R_g \rangle$, of each structure. The average $\langle \dots \rangle$ was carried out over an ensemble of one hundred different DLSP configurations. The radius of gyration is expected to scale as [9,10],

$$R_g \sim AN^v(1 + aN^\delta + bN^{-\eta}), \tag{1}$$

where N represents the number of monomers in the branched-polymer, the exponent v , is related to the fractal dimension of the structure as, $v = d_f^{-1}$, and the terms aN^δ and $bN^{-\eta}$ represent the corrections to scaling. These corrections are characterized by the exponents δ and η . In Fig. 6 we show on a log–log scale the average of the radius of gyration as a function of the number of monomers for each branched structure. These results suggest that there may be corrections to the scaling behavior, $R(r) \sim N^v$. To calculate these corrections to scaling we proceeded as follows: We fitted the radius of gyration data to the nonlinear function:

$$R_g = a_0N^v + a_1N^{a_2} + a_3N^{a_4} = AN^v(1 + aN^\delta + bN^{-\eta}) \tag{2}$$

with $A = a_0$, $a = a_1/a_0$, $b = a_3/a_0$ and the exponents, $\delta = a_2 - v$ and $\eta = a_4 - v$. Starting with the values of v obtained from the analysis of the monomer–monomer correlation functions we carried out a series of five

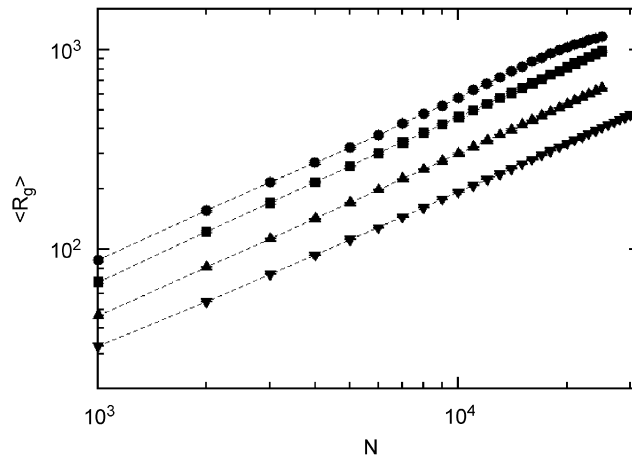


Fig. 6. Scaling behavior of the average of the radius of gyration. The results correspond to structures with one (\circ), three (\blacksquare), six (\blacktriangle) and twelve (\blacktriangledown) branches, respectively. The dashed lines are a guide to the eye.

parameter, a_k ($k = 0, 1, 2, 3, 4$), nonlinear fits to the function defined in Eq. (2) until we obtained a minimum value of the χ^2 merit function. This function is defined as

$$\chi^2 = \sum_{i=1}^N \left(\frac{R_g^i - R_g(a_0, a_1, a_2, a_3, a_4)}{\sigma_i} \right)^2 \quad (3)$$

with R_g^i the data points, σ_i their corresponding standard deviations and $R_g(a_1, a_2, a_3, a_4)$ is the function defined in Eq. (2). The results of this nonlinear fit analysis to the data for the radius of gyration obtained from the simulations are summarized in the following table.

p	A	ν	a	δ	b	η
1	0.25935	0.818(5)	6.4835×10^{-3}	0.2294	4.0163	3.5808
3	0.26047	0.8127(5)	5.4184×10^{-3}	0.2249	3.9927	3.5757
6	0.18029	0.802(5)	4.1666×10^{-4}	0.4976	5.7774	3.5648
12	0.12939	0.7931(5)	6.809×10^{-4}	0.3582	8.0500	3.5564

The digits in the parenthesis after the value of the exponent ν represent the uncertainty which is related to the step-size chosen to obtain the minimum of the χ^2 merit function. We do not quote explicitly the statistical uncertainties of the other fitted parameters because they are of the order of the last digit. With regard to the quality of the results obtained from the nonlinear fits it is important to indicate that in all the cases listed in the table the correlation coefficient of the fit was equal to one and the RMS percent error was of the order of 10^{-6} .

From the above results we can calculate the fractal dimensions of each branched structure as, $d_f = 1/\nu$. Thus, we obtain for the linear chain, $d_f = 1.222(7)$, for the three-arm polymer, $d_f = 1.2305(8)$, for the six-arm structure, $d_f = 1.247(8)$ and for the twelve arm polymer, $d_f = 1.261(8)$. The digit in parenthesis indicates the magnitude of the uncertainty of the fractal dimension that was calculated from the uncertainty of the exponent ν . These results for d_f are more precise than those obtained from the monomer–monomer correlation functions. They suggest that as the number of arms in the structure increases, the fractal dimension of the DLSP also increases within the error bars estimated from the nonlinear fits.

At this point it is important to stress that the present algorithm grows aggregates with defined topology, that is, with defined number of branching points, number of arms that emanate from each branching point, and number of monomers in each of the branches. This could include for example, star-branched polymers with predefined poly-dispersity of the arms. However, with minor modifications in the algorithm we could

grow aggregates with a topology not fully defined in advance. For instance, if we chose as a *target* monomer any of the free ends of the arms, instead of a specific one, then the algorithm would produce a poly-disperse structure. Nonetheless, in this case the poly-dispersity would not be defined in advance but it would be a consequence of the random nature of the aggregation.

4. Conclusions

In conclusion, we have introduced a diffusion-based numerical algorithm to construct simple two-dimensional branched polymers with a relatively large number of monomers. The algorithm excludes closed loops and appears to work for a branching number that is not too large. This procedure yields quenched structures with configurations that are more stretched as compared to their fully thermodynamically equilibrated counterparts. This appears to be due to the directed process used to build them up. From the evaluation of the monomer–monomer correlation functions we were able to estimate the fractal dimension of the branched structure. To get a more precise estimate of these fractal dimensions we carried out a finite size scaling analysis of the radius of gyration. The results obtained appear to suggest, within the estimated error bars, that as the number of arms in the structure increases its fractal dimension also increases slightly. In future work we expect to extend these procedure and analysis to structures with different topologies, as for example, dendrimers, stars with polydispersed arms, and other kinds of hyperbranched structures in two and three dimensions.

Acknowledgments

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