Diffusion-limited star-branched polymers

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We present an algorithm for constructing polymers with defined branching structure and whose morphology is determined by diffusion. We apply this procedure to the construction of star-branched polymers, and we calculate their fractal dimension. This algorithm may be useful for building large branched polymers near their relaxed configurations, which in turn may help determine the properties of the equilibrium configurations of dilute solutions made of these polymers.

Keywords: Star-branched polymers; diffusion-limites aggregates.

En este trabajo presentamos un algoritmo para construir polímeros con una estructura ramal predeterminada y cuya morfología está determinada por procesos difusivos. Aplicamos este procedimiento para construir polímeros de estrella con distintos números de brazos y calculamos su dimensión fractal. Este algoritmo puede ser útil para construir polímeros ramificados de gran tamaño cerca de sus configuraciones de equilibrio, lo cual a su vez puede ayudar a determinar las propiedades de los estados de equilibrio de soluciones diluidas hechas de estos polímeros.

Descriptores: Polímeros de estrella; agregados limitados por la fusión.

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1. Introduction

The properties of star-branched polymers have been studied using a variety of methods, both experimentaly and theoretically [1, 2]. Such systems are interesting from the theoretical point of view because the understanding of the details of the structure should help in predicting important properties of polymeric systems on a macroscopic scale, such as viscoelasticity. Star-branched molecules are nice stepping-stone model objects for studying systems in which the topology of the molecules plays an important role. Such objects often exhibit properties different from their linear counterparts; the differences are mostly caused by the nonuniform density of stars as well as by the interactions between the arms. During the last two decades, some simple computer models star-branched polymers have shown how these structures are made up and have pointed out the differences between static and dynamic properties when compared with linear chains [3]. However, these studies are limited since a small number of arms as well as a small number of monomers were considered, and they were usually done on a lattice. The main difficulty is to relax efficiently these polymeric structures with several branches and a relatively large number of monomers due to steric effects.

The purpose of this work is to introduce a novel numerical algorithm based on a diffusive procedure to build up efficiently two-dimensional star-branched polymers made of several branches and many thousands of monomers. This algorithm produces quenched structures that are not in a fully equilibrated configuration. Nonetheless, it permits the

growth of very large structures that appear to have a slightly larger fractal dimension than their thermodynamically equilibrated counterparts obtained with a much lower total of monomers (lass than one thousand). This means that the configurations obtained are expected not to be very different from their equilibrated counterparts and may be useful in approximately determining the physical properties of the equilibrated structures.

2. Construction of the diffusion-limited star-branched polymers

Here we will present the algorithm for constructing a diffusion-limited star-branched polymer (DLSP) in two dimensions. First, we propose the branching topology of the desired DLSP, that is, we define the number of arms or branches that the star polymer will have. For example, in Fig. 1 we show the topology of a DLSP with three branches. The monomers are conveniently numbered so that a given monomer is linked to a target monomer. In the example 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. All N monomers of the structure are linked to a specific target monomer. Once the topology is defined and the monomers are numbered, the building procedure starts with a monomer of diameter a located at the origin. This is the seed monomer and it is numbered 1. Then, we release a second monomer from a circle of arbitrary radius centered at the tar-

get monomer as sketched in Fig. 2. This monomer is allowed to move randomly until it reaches the target monomer, in which case it is attached to it at the contact point. Successive identical particles are attached to the aggregate in the same way. That is, once the structure has been partially grown, the next numbered monomer is released from a random point on a circular shell of arbitrary radius centered at the respective target monomer. This monomer moves randomly until the distance between the released particle and any of the other particles of the aggregate happens to be less than a; then, the released particle is "killed" and a new one with the same number is released. Only in the case in which the incoming particle is close to the target particle (within a distance less than a) the particle sticks to its target particle at the contact point and a new one with the next number is released. If the particle moves to a distance too far away from the aggregate, this particle is also "killed" and a new one, with the same number, is released. To speed up the simulation we used a step-size control based on a recursive procedure to permit a rapid approach of the particle to the aggregate without hindering large excursions [4]. In all simulations the "killing" disc had size $2r_{max}$, where r_{max} is the farthest distance between the origin and the monomers of the cluster.
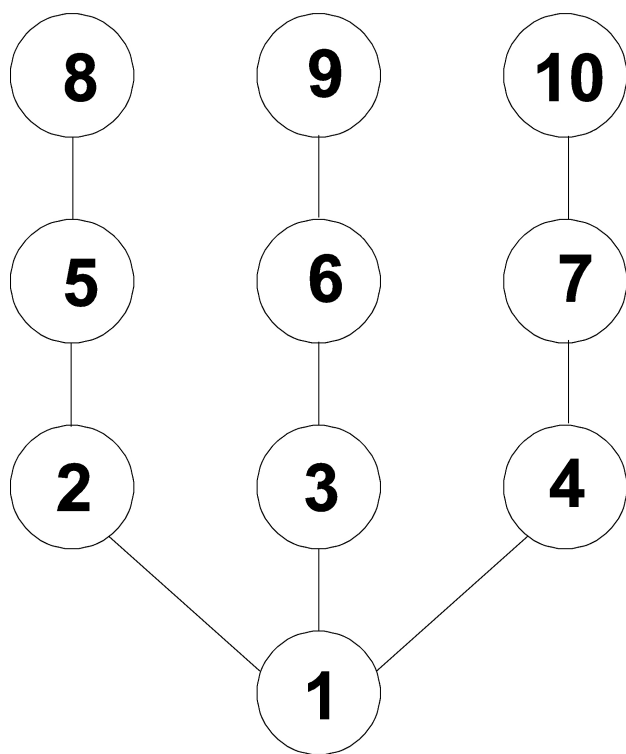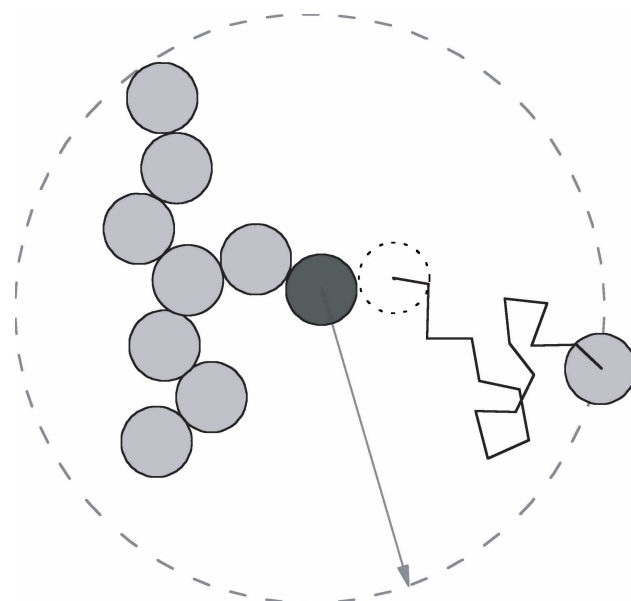

FIGURE 2. Sketch that shows the procedure for building a DLBP. The black disc represents the target monomer.

3. Results

In Figs. 3a, b, c, and d, we show typical configurations of the DLSP obtained using the algorithm described in the previous section for star-branched polymers with $p = 1$, 3, 6, and 12 arms and $N = 10,000$ monomers. We observe that the arms of the branched structures are wiggled due to the diffusive process used to build them up. In order to make a quantitative estimate of the compactness of the structures, we calculated their fractal dimension from the particle-particle correlation functions of the aggregates. This is done by the usual histogram method [5].

From a randomly chosen monomer, the distances r to all other monomers are calculated, and the histogram $N(r, \Delta)$ of the distance distribution is obtained by counting the number of distances in the interval $(r, r + \Delta)$. The histogram is further averaged after all the monomers of the aggregate are swept and for a number of different DLSP configurations. The pair-correlation function for two-dimensional objects is then obtained by means of the formula, $g(r) = N(r, r + \Delta)/(2\pi r \Delta)$. Finally, from the curves for $g(r)$ versus r, we extracted the fractal dimensions by obtaining the slopes of the linear regions of the curves and using the formulae $d_f = 2 + $slope, with d_f the fractal dimension. In order to exemplify the procedure, in Fig. 4a, b, c, and d we show the pair-correlation function for star-branched polymers with $N = 10,000$ monomers and $p = 1$, 3, 6, and 12 arms, respectively. These results were obtained by averaging over 10 different DLSP configurations. In this case the fractal dimensions obtained were $d_f = 1.22 \pm 0.01$, $d_f = 1.25 \pm 0.01$, $d_f = 1.25 \pm 0.01$, and $d_f = 1.35 \pm 0.01$, for $p = 1$, 3, 6, and 12, respectively. As expected, as the number of branches increases, the structure becomes more compact. This is more clearly shown in Fig. 5 where we have plotted the pair-distribution

FIGURE 1. Schematic sketch of the topology of a three-arm star polymer.
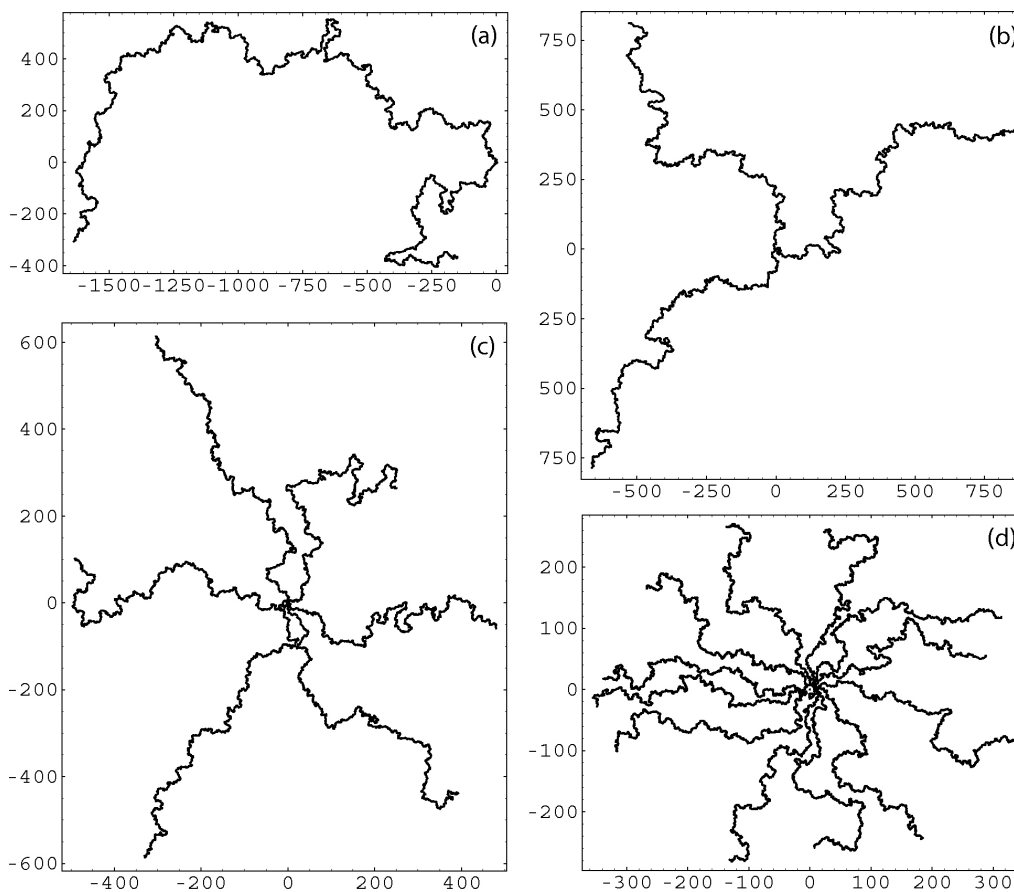
FIGURE 3. Typical configurations of DLSP. (a) single-arm star or equivalently linear polymer, (b) three-arm star polymer, (c) six-arm star polymer, and (d) 12-arm star polymer.
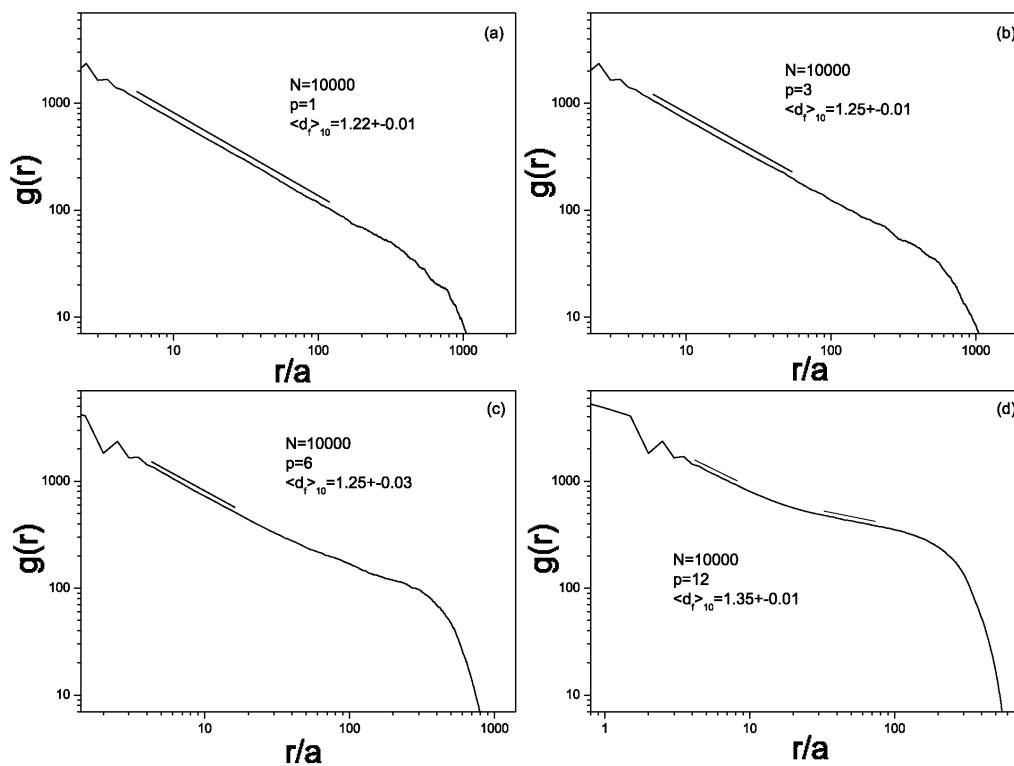

FIGURE 4. Pair-distribution function for (a) $p = 1$, (b) $p = 3$, (c) $p = 6$, and (d) $p = 12$ arm DLSP. Straight lines represent the slopes of the linear regions from which the fractal dimensions are obtained.
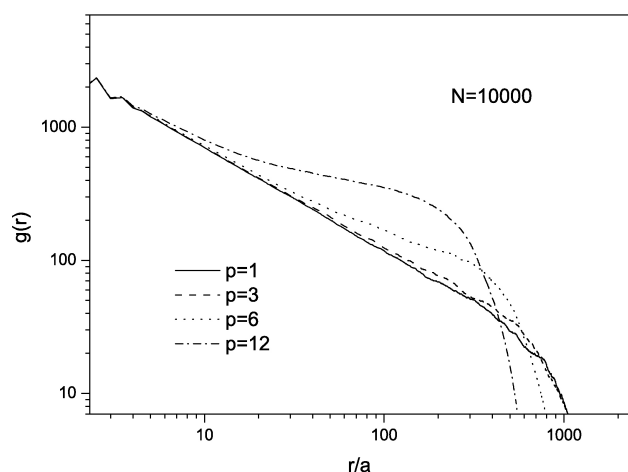
FIGURE 5. Pair-distribution functions for all the DLSP considered.

functions for all the DLSP considered. Notice that not only the fractal dimension of the star increase as the number of branches increases, but, a second linear region also shows up for the star with 12 arms. However, this second linear region is related to the average density profile rather than to the fractal dimension of the structure [6]. For stars with a very large number of arms, this second region should appear more clearly. We should notice that the fractal dimensions obtained for the DLSP structures of this paper are systematically smaller than their thermodynamically equilibrated counterparts. That is, if we considered polymers with the same branched structure but in which the monomers can move freely maintaining the connectivity and avoiding overlapping, their fractal structure would be larger than that obtained here. For example, for a two-dimensional self-avoiding walk linear polymer the fractal dimension is 1.33,

a value larger than 1.22, the value obtained for the equivalent diffusively-built linear structure. Also, we can compare our results with those of Ref. 7, where equilibrated star-branched polymers with $p = 3$ arms were considered but embedded in a three-dimensional space. In this case the fractal dimension of very small aggregates with a maximum of 799 monomers was $d_f = 1.2$. The star-branched polymers considered in the present paper are made of $N = 10,000$ monomers, which is enough to show that the algorithm to construct the DLSP works properly. However, the procedure can easily handle much larger structures in a reasonable computation time.

4. Conclusions

In conclusion, we have proposed a diffusion-based numerical algorithm to construct branched polymers with any desired topology and total number of monomers, as long as the branching is not too high, and excluding closed loops. We exemplified the procedure with the construction of a number of star-branched polymers. This mechanism produced quenched structures in states that are more stretched than their thermodynamically equilibrated counterparts. This is due to the directed process used to build them. In the near future we will extend these results to include structures with different topologies like dendrimers, stars with polydispersed arms, and other kinds of hyperbranched structures in both two and three dimensions.

Acknowledgments

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