Number of arm selection in two-dimensional diffusion processes

C.I. Mendoza\textsuperscript{1,a} and G. Ramírez-Santiago\textsuperscript{2}

\textsuperscript{1} Departamento de Polímeros, Instituto de Investigacines en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, 04510 México, D.F., Mexico

\textsuperscript{2} Departamento de Física-Química, Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, 01000 México, D.F., Mexico

Received 17 April 2008 and Received in final form 29 May 2008
Published online: 23 July 2008 – \copyright EDP Sciences / Società Italiana di Fisica / Springer-Verlag 2008

Abstract. We introduce an algorithm to generate two-dimensional diffusion-limited star-branched aggregates (DLSA) attaching bi-functional monomers successively to a central colloidal particle with any desired number of reactive sites. The proposed algorithm produces star-shaped aggregates that grow forever and show a power law polydispersity in the chemical length of the arms near the central colloid. More interestingly, it gives rise to a number of arm selection consisting in that only a small number of arms (around five) define the final structure at relatively large distances from the central colloid, independently of the initial number of reactive sites and the size of the central colloid. We characterize the structure of the aggregates by means of the particle-particle correlation function, analyze its scaling properties and obtain the fractal dimension.

PACS. 61.43.Hv Fractals; macroscopic aggregates (including diffusion-limited aggregates) – 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 82.70.Dd Colloids

1 Introduction

Considerable attention has been focused on the question of how to describe the configuration of both linear and branched polymers \cite{1}. Although most models are based on the concepts of equilibrium statistical mechanics \cite{2}, in the case of linear polymers, models based on the nonequilibrium diffusion-limited aggregation (DLA) have been devised \cite{3–6}. The primary interest in this kind of models is that they lead to self-avoiding walks (SAWs) which grow forever. The construction of such a walk is of great physical importance in connection with the kinetics of irreversible growth processes such as polymerization and kinetic gelation. Two-dimensional versions of these models have also been used to describe submonolayer vapor-deposition polymerization \cite{7} and diffusion-limited polymerization mechanisms have been applied to the problem of surface growth \cite{6} and in situ polymerization \cite{8}. In these models, many chains grow from a line or plane of active sites to represent growth from a surface. Similarly, more sophisticated models have been introduced to describe growth of polymers having higher-order connectivity \cite{9}. However, no such models have been applied to the specific case of star-branched polymers or aggregates. That is, no related models have been proposed to describe the growth of many chains from a central colloidal particle.

The subject of this letter is to propose a kinetic mechanism to grow star-branched aggregates that are fully determined by diffusion. We consider specifically the case of two-dimensional growth and found that these diffusion-limited star-branched aggregates (DLSA) grow indefinitely, are self-avoiding and contain arms with a distribution of lengths. More interestingly, the large-scale structure of the aggregate is determined by only a small amount of arms (around five) independently of the size and the number of active sites of the central colloidal particle. The model is an interesting cross between SAWs, DLA, and star polymers.

2 Model

We start the construction of a DLSA in two dimensions with a central colloidal particle of radius $R_c$ with $f$ equidistant reactive sites as shown in Figure 1. Then, an incoming bifunctional monomer is released from a random point far away from the central colloid. This monomer moves in random directions in steps of size equal to its diameter $a$. When the distance of this monomer to any reactive site is less than its diameter, then it is attached to the reactive site at the contact point. Successive monomers are incorporated to the aggregate in a similar way, \textit{i.e.}, the incoming monomer is attached to a reactive site of the central colloid or to the monomer located at the end.
The European Physical Journal E

Central colloid

Incoming monomer

Reactive sites

Fig. 1. Schematic drawing of the aggregation process to build diffusion-limited star aggregates (DLSA). In the figure the number of reactive sites is \( f = 8 \).

of any branch of the aggregate. Since the monomers are bifunctional, no additional branching points are generated. We adopt absorbing boundary conditions at the inactive (nongrowing chain) sites. This means that when an incoming monomer touches either the central colloid or the aggregate at a point that is not reactive, including all the monomers that are not located at the end of any branch, then the incoming monomer is discarded and a new one is released. By iterating this procedure, consecutive monomers are released and eventually attached to the original aggregate. In this way, the algorithm produces star-branched structures of \( N \) monomers and with \( f \) polydisperse arms. Since the incoming monomers diffuse to the growing tips from faraway, there must always be a path from the tips to infinity that does not touch the aggregate. Therefore, this growing mechanism produces structures that grow endlessly. This growing procedure is summarized in Figure 1.

3 Results

In what follows, we utilize this model to construct aggregates made of up to \( N = 50000 \) monomers and \( f = 3, 6, 12, 18, 24, 30, 100, \) and 200 reactive sites in the central colloid. The radii of the central colloid were \( R_c = 25, 50, 100, \) and 200 monomer diameters. Averages over 200 different realizations of the aggregates for the values of \( f \) and \( R_c \) indicated above were performed. A typical configuration is shown in Figure 2 for an aggregate with \( f = 100 \) reactive sites and \( R_c = 100a \). The large-scale structure of this aggregate seems to show only few surviving arms. In the inset we show an early stage of formation of the aggregate showing the large initial number of arms. It can be seen that the structures generated by the algorithm are stars whose arms have a distribution of lengths. An analysis of this polydispersity is shown in Figure 3 where the histograms showing the number of monomers per arm are plotted against the arm number. The arms were numbered according to its chemical length, that is, the first arm is the one that has the largest number of monomers, the second arm is the one with the second largest number of monomers and so on. In other words, the arm number represents the rank of an arm with respect to its mass. In all the cases the histograms show clearly three different regions. The first region (labeled F), the transition region (labeled T), and the corona (labeled C). In the corona region, near the central colloid, the chemical length of the arms shows a power law scaling of the form \( N_i \sim (R_c/a)^4/3i^{-\alpha} \). For \( f = 100 \) the value of the exponent \( \alpha \) is \( \alpha \simeq 1.83 \). The hump indicates that around five arms grow more than the others. The vertical dotted lines indicate the border between the different regions. The inset shows the same but for \( R_c/a = 25 \) and different values of \( f \). The corona is not yet fully developed for a small number of reactive sites \( f \). To guide the eye, we have also plotted a straight line with a slope \(-1.83\).