

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/229008372>

Spheres Growing on a Sphere: A Model to Predict the Morphology Yields of Colloidal Molecules Obtained through a Heterogeneous Nucleation Route

ARTICLE *in* LANGMUIR · JULY 2012

Impact Factor: 4.46 · DOI: 10.1021/la301857h · Source: PubMed

CITATION

1

READS

23

11 AUTHORS, INCLUDING:



Antoine Thill

Atomic Energy and Alternative Energies Com...

74 PUBLICATIONS 1,308 CITATIONS

SEE PROFILE



Elodie Bourgeat-Lami

CPE Lyon

167 PUBLICATIONS 5,401 CITATIONS

SEE PROFILE



Olivier Spalla

Atomic Energy and Alternative Energies Com...

115 PUBLICATIONS 2,824 CITATIONS

SEE PROFILE



Etienne Duguet

French National Centre for Scientific Research

155 PUBLICATIONS 5,180 CITATIONS

SEE PROFILE

Spheres Growing on a Sphere: A Model to Predict the Morphology Yields of Colloidal Molecules Obtained through a Heterogeneous Nucleation Route

Antoine Thill,^{*,†} Anthony Désert,[‡] Sarah Fouilloux,[†] Jean-Christophe Taveau,[§] Olivier Lambert,[§] Muriel Lansalot,^{||} Elodie Bourgeat-Lami,^{||} Olivier Spalla,[†] Luc Belloni,[†] Serge Ravaine,[⊥] and Etienne Duguet[‡]

[†]CEA Saclay, IRAMIS, Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire, 91191 Gif sur Yvette, France

[‡]CNRS, Université Bordeaux, ICMCB, 33600 Pessac, France

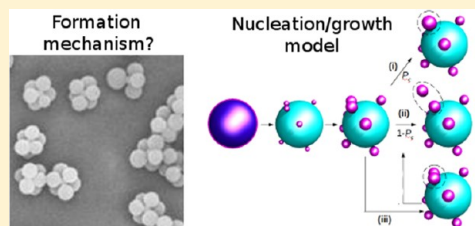
[§]CNRS, Université Bordeaux, CBMN, 33600 Pessac, France

^{||}Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 69616 Villeurbanne, France

[⊥]CNRS, Université Bordeaux, CRPP, 33600 Pessac, France

W Web-Enhanced Feature **S** Supporting Information

ABSTRACT: Through the heterogeneous nucleation of polymer nodules on a surface-modified silica particle, the high-yield achievement of hybrid colloidal molecules with a well-controlled multipod-like morphology was recently demonstrated. However, as the formation mechanism of these colloidal molecules has not been completely understood yet, some opportunities remain to reduce the tedious empirical process needed to optimize the chemical recipes. In this work, we propose a model to help understand the formation mechanism of almost pure suspensions of well-defined colloidal molecules. The outcomes of the model allow proposing probable nucleation growth scenario able to explain the experimental results. Such a model should make easier the determination of the optimal recipe parameters for a targeted morphology. The reasonably good agreements between the model and the experimental results show that the most important processes have been captured. It is thus a first step toward the rational design of large quantities of chemically prepared colloidal molecules.



INTRODUCTION

Finding an efficient route for the simple, reproducible, and high yield synthesis of well-defined hybrid nonspherical colloids remains a great challenge. Indeed, these kinds of particles may participate in the development of new hierarchical materials with potential interesting optical properties.^{1,2} Such morphologies have been called “colloidal clusters” or “colloidal molecules” due to their shape analogy with simple molecules.^{3–5} Among the possible routes that have been explored to obtain such colloidal molecules, few reach both controllable and well-defined morphology and easy production of large amounts.⁶ The formation of polymer particles at the surface of well-defined inorganic colloids has been shown to be an efficient route toward a vast family of different hybrid morphologies.^{6–10} Indeed, the heterogeneous nucleation of polystyrene in the presence of monodisperse and surface-modified silica seeds appeared to be a very promising route toward a combined efficacy (shape control, large production). Reculosa et al. first performed the seeded-growth emulsion polymerization of styrene in the presence of surface-modified silica nanoparticles and obtained a controlled number of

polymer nodules (5 or between 6 and 8) per silica seed when the seed size was changed from 80 to 170 nm.^{11–13} This was systematically explored by Perro et al.¹⁴ who were able to produce morphologies of clusters having from 2 to 12 polystyrene nodules by a continuous size change of the silica seed modified by methacryloxymethyltriethoxysilane (MMS). Recently, the recipe was further optimized to reach completed monomer-to-polymer conversions, higher morphology yields (as high as 80% for tetrapods, hexapods), and production at the gram scale.¹⁵ However, the morphology yields are still limited for some morphologies, and the mechanism controlling the change in morphology as a function of some synthesis parameters remains not clearly established.

The ultimate goal of a model for such heterogeneous nucleation would be the ability to predict the obtained morphologies and their proportion for a given set of synthesis parameters. To predict the obtained morphologies using the

Received: May 7, 2012

Revised: July 3, 2012

Published: July 10, 2012

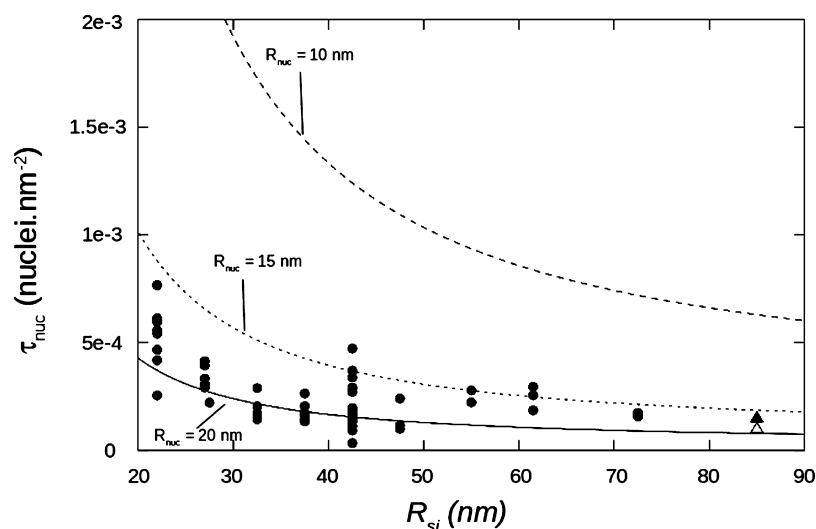


Figure 1. Evolution of the calculated τ_{nuc} values as a function of the silica seed size, as estimated from previously published data. Black dots correspond to the minimum nucleation rates based on experimental observations for all synthesis by Perro et al.¹⁴ and Désert et al.¹⁵ The open triangle corresponds to the early stage TEM observations of Reculosa et al.¹² The black triangle shows the τ_{nuc} value deduced from cryo-TEM observation.¹² The lines correspond to a nucleation surface density computed according to eq 1 with $h_c = 100$ nm, $k = 10^{-2}$, and a R_{nuc} of 10, 15, and 20 nm, respectively (see text).

synthetic approach described above, Perro et al. have proposed a model to explain the growth of attached nuclei on the surface of the silica seeds.¹⁴ It is based on a work by Battye et al. who proposed to combine an attractive potential between a central particle and spherical satellites and a repulsive potential between the satellites to predict the possible morphologies as a function of the relative particle sizes.¹⁶ This model was successfully used to understand the experimental results, but it relies on a calibration parameter K . With the last optimized recipe, the calibration parameter appeared to change.¹¹ These changes are difficult to predict or to link to physicochemical processes of the nucleation and growth. In an attempt to get rid of calibration parameters, we propose an extension of such a model (based only on simple geometrical concepts) that allows understanding of how the various morphologies occur and how their yield evolves as a function of the proportion of the reactive species during the synthesis. Such a model would be a valuable tool not only to understand the underlying mechanism but also to set new ideas toward a generic efficient recipe for the synthesis of colloidal molecules.

MODEL DESCRIPTION AND HYPOTHESIS

Our goal is to develop a model able to predict the hybrid particles morphologies obtained during the heterogeneous nucleation of a polymer on the surface of a colloidal seed based only on simple geometric rules. Although, the predictions of the model were compared to polystyrene on MMS-grafted silica seeds (see later), the model should be useful for many other different experimental systems.

The Nucleation Stage. In the present model, we make the assumption that the nucleation is purely heterogeneous. However, the proposed model does not try to precisely describe the heterogeneous nucleation process. It is only based on geometrical considerations. We consider the colloidal silica seeds introduced at the beginning of the reaction as perfect spheres of radius R_{si} . The size of the initial surface nuclei R_{nuc} is given as a starting parameter. The number of initial nuclei is controlled by the nuclei surface density τ_{nuc} . Considering an initial fixed number of nuclei ($N_{\text{nuc}} = 4\pi R_{\text{si}}^2 \tau_{\text{nuc}}$) of identical

radius means that we assume separate nucleation and growth stages. We make here the assumption that all surface nuclei appear with the same size. As the initial nuclei are small compared to the final nodule size, the potential initial polydispersity therefore has a small effect on the final morphologies. We also assume no secondary nucleation and no continuous nucleation. Therefore, after the nucleation stage, all the small polymer chains reaching the growing hybrids are captured by the existing nuclei before being able to nucleate new particles.

To estimate the boundaries of the nucleation surface densities that should be used in order to predict the heterogeneous nucleation and growth of polymer nodules on silica, the available experimental data on the nucleation stage were used. Indeed, there exist several experimental proofs that would allow one to assess a range of τ_{nuc} values. Reculosa et al.,^{11–13} Perro et al.,¹⁴ and Désert et al.¹⁵ performed the emulsion polymerization of styrene at a concentration of 100 g·L⁻¹ in the presence of silica seeds. The silica seeds were previously modified by the use of MMS at a low nominal surface density (from 0.1 to 0.5 MMS·nm⁻²). Using size data from transmission electron microscopy (TEM) observations of the obtained latex particles and the weight of dried extracts, it was possible to give the ratio of the final number concentration of polystyrene spheres N_{ps} and silica seeds N_{si} . Together with the knowledge of the silica seed radius, this can be used to obtain a minimum value of $\tau_{\text{nuc}} = N_{\text{ps}} / (4\pi R_{\text{si}}^2 N_{\text{si}})$ using the assumption that every latex particle was once a surface nucleus. This only gives an underestimate of the actual nucleation surface density because using the final nucleus number does not allow taking into account potential coalescence events. Short-term experimental data are necessary to provide some unbiased nucleation rates. Reculosa et al. also showed TEM images at the beginning of the growth (15 min) for 170 nm silica seeds.¹² Counting the number of nuclei at this early stage gives a probable nuclei surface density of $\tau_{\text{nuc}} = 10^{-4}$ nuclei/nm². Taveau et al. confirmed these observations at early polymerization times by cryo-electron tomography.¹⁷ All these

calculated τ_{nuc} values as a function of the silica seed size are shown in Figure 1.

In Figure 1, a spread of the experimental data is observed. It is probably due to the fact that it mixes experiments with changes in the total concentration of silica seeds and in surfactant(s) used to stabilize the suspension. Indeed, while Reculosa et al.^{11–13} and Perro et al.¹⁴ used Synperonic NP30 surfactant during the synthesis to stabilize the hybrid latex suspension, Désert et al.¹⁵ used a mixture of 95/5 (wt./wt.) of Synperonic NP30/sodium dodecylsulfate and MMS surface grafting density of 0.5 function-nm⁻². It is most likely that the nucleation surface density is affected by these changes.

A clear size effect is noticed in Figure 1: the smallest seeds have a higher nucleation surface density than the largest. It is possible to explain this if a two-step process is assumed for the formation of the surface nuclei. At very early stage, one may assume the presence of a layer of oligomers at the surface of the silica seed. When this layer reaches a critical thickness or concentration, the nucleation phenomenon occurs, leading to the formation of surface nuclei. If we consider that all the oligomer chains in this layer contribute to the formation of N_{nuc} surface nuclei, the mass conservation gives (see Supporting Information for details):

$$\tau_{\text{nuc}} = \frac{N_{\text{nuc}}}{4\pi R_{\text{si}}^2} = \frac{kR_{\text{si}}}{4\pi R_{\text{nuc}}^3} \left[\left(1 + \frac{h_c}{R_{\text{si}}} \right)^3 - 1 \right] \quad (1)$$

where k accounts for the ratio in equivalent densities of the oligomers layer and the surface nuclei, and h_c is a critical thickness at which the oligomers layer transformed into surface nuclei of size R_{nuc} . The parameters $k = 10^{-2}$, $h_c = 100$ nm, and $R_{\text{nuc}} = 20$ nm allow to describe roughly the experimentally determined minimum nucleation surface density. Two higher nucleation surface densities were considered by decreasing R_{nuc} from 20 nm to 15 and 10 nm, respectively. On the surface of the seed, the N_{nuc} nuclei are initially placed at random positions. The only other constrain is that the nuclei do not touch each other initially.

The Growth Stage. Taveau et al.¹⁷ observed by cryo-electron tomography that the latex satellite particles grow with a fixed contact angle on the surface of the silica seed. According to the experimental TEM observations and especially the final morphologies, a very low wetting of the seed surface seems to be a reasonable approximation. Therefore, in this Article, the study is restricted to the simplest case of a 180° contact angle. At the end of the nucleation stage, the surface nuclei are considered to lie on the silica seed. Upon growth, the center of the growing nuclei is moved away from the silica seed in order to maintain contact. The position of the nuclei is therefore such that the distance between the nuclei and seed center always equals to $R_{\text{si}} + R_{\text{nuc}}$. After this initial placement of all the nuclei, the volume of polymer per seed is $V_p(0) = (4\pi R_{\text{si}}^2 \tau_{\text{nuc}})(4/3\pi R_{\text{nuc}}^3)$ in the case of 180° contact angle. The volume of seed is $V_{\text{si}} = 4/3\pi R_{\text{si}}^3$, which give an initial volume ratio of $R_v(0) = V_p/V_{\text{si}} = 4\pi \tau_{\text{nuc}} R_{\text{nuc}}^3 / R_{\text{si}}$. The rest of the simulation consists in growing all the nuclei at the same surface rate until all the monomer molecules have been converted into polymer. In the rest of the article, the growing nuclei are called “nuclei” for simplicity. At each simulation step, the mass of all nuclei is thus increased according to

$$\Delta m \sim K_g R_{\text{nuc}}^2 \quad (2)$$

The value of K_g is initially fixed such that, during a simulation step, the radius of the largest nuclei is changed by a small chosen increment. The growth is continued until the system reaches the final value of the volume ratio R_v . Using such growth law throughout the simulation, we neglect possible modifications at high surface coverage where the whole surface of the nuclei is not easily accessible for the monomers.

If, in the course of the growth process, two nuclei happen to touch each other, then three possibilities are introduced in the model to deal with the situation: (i) the two nuclei merge by coalescence as a new nucleus of size $(R_{\text{nuc1}}^3 + R_{\text{nuc2}}^3)^{1/3}$; (ii) one of the two nuclei is expelled from the seed; (iii) one of the nuclei pushes the other on the surface of the seed in order to prevent (i) or (ii). The solution (ii) is possible even in crowded seeds where many nuclei are almost in contact. Indeed, the expulsion of one nucleus does not lead to any new contact. In the case of coalescence (i), new contact may be induced by the coalescence event. This can lead to a cascade of coalescence events in crowded environments. Coalescence and expulsion create new free space on the surface of the seed for further growth of the nuclei. When nuclei push each other (iii), it does not create new free space at the surface. It modifies only the nuclei arrangement in order to find a configuration that would fit on the silica seed without contacts. In the case of (iii), it is likely that the pushed nucleus will then touch a third nucleus especially in a crowded seed. To deal with the possibilities of such cascade contacts, a recursive algorithm was adopted. The pushed nucleus pushes the new nuclei it touches starting from the closest until no contact remains. When the nuclei growth has reached a point where no possible configurations exist anymore, this algorithm will induce infinite motions of the nuclei. To prevent infinite motions from occurring while allowing the efficient approach of the maximum packing, a stopping condition is introduced. This stopping condition is chosen by comparing the packing limits reached by our recursive algorithm to the previous results of Mansfield et al.¹⁸ Using the rule that no particle should be moved more than 20 times in our recursive motion process allows both an efficient computational scheme and a good approach of $R_v^{\text{max}}(n)$ (see Table 1 in the Supporting Information). When the stopping condition is fulfilled, solution (i) or (ii) is applied to free some surface space on the seed. To choose between (i) or (ii), a coalescence probability P_c is used, $1 - P_c$ being the expulsion probability. P_c can be a function of the conversion. Indeed, when the nuclei are in the presence of many monomer molecules, the polymer is still liquid-like, and, in this case, coalescence is more likely. On the contrary, at the end of the polymerization (i.e., at high conversion), when almost all monomers are incorporated into quite rigid nodules, the coalescence is less likely. To our knowledge no accurate theory describing the nuclei coalescence probability as a function of the monomer conversion is available. We choose to define a critical volume ratio between the polymer and the seeds R_{vc} above which P_c starts to decrease from its initial value to zero for complete monomer conversion. If R_{vc} is equal to the final volume ratio R_v , then P_c is constant during the entire reaction. Figure 2 summarizes the model rules for the nucleation and growth.

When the final volume ratio R_v is reached, the number of remaining nuclei, their position, and size are saved for further statistical use. It is important to mention that in process (ii), the expelled nuclei continue to consume monomers at the same

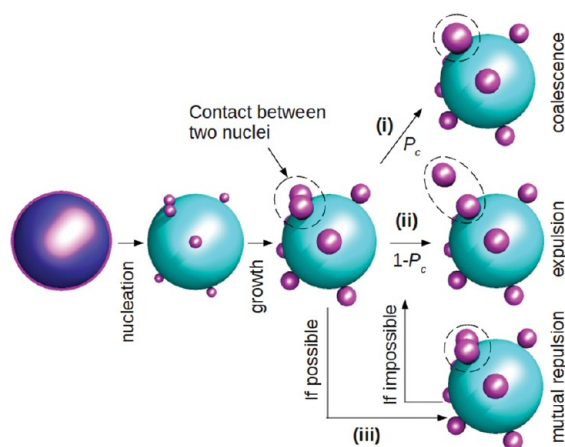


Figure 2. Model rules for the nucleation and growth of the nuclei. Initially, $4 \pi R_{\text{si}}^2 \tau_{\text{nuc}}$ nuclei of size R_{nuc} are randomly placed on the surface of the seed. The various scenarios considered in the case of nuclei contact during the growth are: (i) coalescence, (ii) nuclei expulsion, and (iii) nuclei mutual repulsion. When mutual repulsion is no longer able to find a “non-contact” configuration for the nuclei, (i) or (ii) is applied with probability P_c and $1 - P_c$, respectively.

surface rate as attached nuclei. Thus, they are considered in the computation of the volume ratio $R_v = V_{\text{nuc}}/V_{\text{si}}$.

Lastly, the present model was restricted to the study of the behavior of a single seed or statistical series of single seeds. By doing so, the possible heteroaggregation between growing colloidal molecules was neglected. Such heterogeneous aggregation is, however, sometimes observed in the samples.¹⁵ If the surface coalescence of nuclei belonging to the same seed is possible, then coalescence between nuclei belonging to different seeds could indeed also occur with probabilities controlled by the sample concentration.

■ GEOMETRICAL BOUNDARIES

From the basic rules used in this geometric model, it is already possible to define some obvious boundaries for the possible colloidal molecule morphologies. For example, an infinite growth process is possible for one nucleus or two nuclei attached at opposite poles of the seed without any contact between the nuclei. Thus for colloidal molecules with one or two surface nuclei, no maximum volume ratio between the polymer and the seed exists. As soon as more than two identical nuclei are present on the seed, a maximum polymer volume is expected during the growth at constant contact angle. Above this maximum volume or size ratio, it is impossible to find a configuration maintaining the surface contact of all nuclei. For some simple geometries with nuclei of identical size, this maximum volume ratio R_v^{max} (or nuclei/seed size ratio) can be analytically determined. For three nuclei, the maximum size ratio is given by placing the seed in the middle of the space left by just touching three identical nuclei. Simple geometry gives a maximum size ratio of this arrangement: $(R_{\text{nuc}}/R_{\text{si}})_{\text{max}}(3) = \cos(\pi/6)/(1 - \cos(\pi/6)) = 6.4641$, which corresponds to a maximum volume ratio between the polymer and the seed of $R_v^{\text{max}}(3) = 3 (\cos(\pi/6)/(1 - \cos(\pi/6)))^3 \sim 810.3$. Computing the maximum volume ratio (or size ratio) can be performed for simple spheres assemblies having 3, 4, 6, 8, or 12 nodules. The maximum size ratio and corresponding maximum volume ratio for these simple cases are given as Supporting Information.

A numerical computation of the maximum coverage of a sphere by spheres having a given size ratio was published by Mansfield et al.¹⁸ The line in Figure 3A presents the maximum volume ratio achievable for a number of nodules N_{nuc} going from 3 to 21 using Mansfield et al. results. We used the present model to compare with the Mansfield results and to extend them for $N_{\text{nuc}} > 20$. We used the mutual repulsion of the nuclei to deal with early contacts for various initial numbers of nuclei. The simulations were stopped when a first nuclei has to detach from the seed or coalesce with another one. The volume ratio at this first event is then averaged over 100 simulated growths. The model correctly reproduces the analytical volume ratio, and it compares very well with the Mansfield results and allows one to extend the $R_v^{\text{max}}(n)$ curve up to large values of n (see Table 1 in the Supporting Information). It is interesting to describe the frontier of the possible existence of a given morphology using a volume ratio $R_v^{\text{max}}(n)$ because it combines both the size and number of the surface nuclei in a single value. Knowing the composition of the reaction medium, the achievable morphologies are given by a vertical line below the $R_v^{\text{max}}(n)$ limit. For example, if $100 \text{ g}\cdot\text{L}^{-1}$ of styrene and $10 \text{ g}\cdot\text{L}^{-1}$ of silica seeds are used, the maximum volume ratio will be about 21, assuming a silica density of $2.2 \text{ g}\cdot\text{cm}^{-3}$ and a polymer density of $1.05 \text{ g}\cdot\text{cm}^{-3}$. It is possible to say that, according to Figure 3A, it is impossible from this composition to obtain more than nine attached nuclei of identical size per seed at the end of the synthesis (see the dotted lines in Figure 3A).

At the beginning of the polymerization process, the volume ratio between the polymer and the seeds is low. As the polymer formation progresses, more and more monomer units are added to the nuclei, and the volume ratio is increasing. If the volume ratio $V_{\text{nuc}}/V_{\text{si}}$ reaches the maximum volume ratio for the number of initially attached nuclei $R_v^{\text{max}}(N_{\text{nuc}})$, there is no more space for further growth of the initially present nuclei, whatever their arrangement on the seed. The more nuclei initially attached on the seed, the sooner this maximum ratio is reached (see Supporting Information for the values). Then, coalescence or expulsion of one nucleus is required if further growth is to occur. This leads to a reduction of the number of attached nuclei. This initial simple discussion already fixes boundaries for the possible morphologies. Indeed, in a synthesis route to produce, for example, pure tetrapods colloidal molecules, if 0.1 cm^3 of seeds is introduced in the reactor, then no more than 35.2 cm^3 of polymer can enter in the composition of these pure tetrapods. Introducing more polymer than this limit will never allow the formation of pure tetrapod suspensions. However, being exactly at or below this maximum boundary does not guarantee success either. Obviously, on one hand, introducing too few monomers will not be successful, and on the other hand, introducing exactly the maximum amount only leaves the possibility of a perfectly arranged tetrapod, which is also not likely. From this general discussion, it appears that most probably an optimal polymer quantity exists for any final desired number of nuclei. The model has to be used to define these optimal values according to different growth scenarios.

Another obvious condition for the successful production of a given morphology according to the present model rules is linked to the nucleation stage. In the case of a single heterogeneous nucleation, it is indeed impossible to get more nuclei at the end of the synthesis than the initial number of nuclei. As all the nuclei appear in the nucleation stage, if three nucleation sites are initially present on the seed, it will be

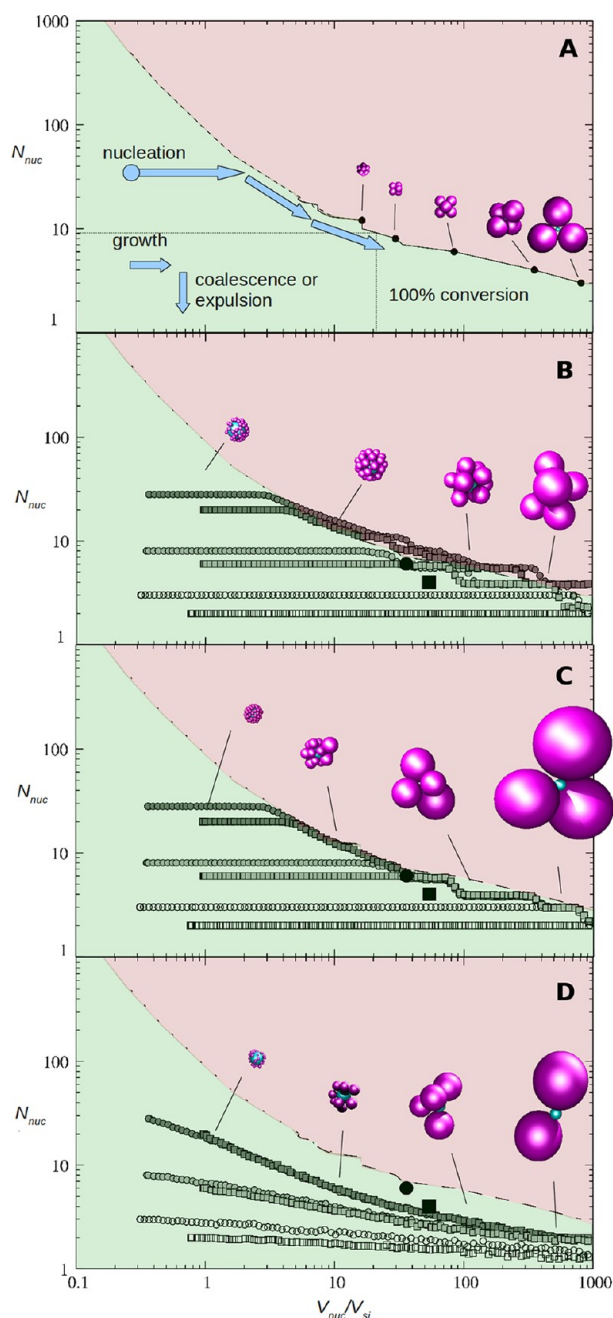


Figure 3. Evolution of N_{nuc} as a function of V_{nuc}/V_{si} . The limit $R_v^{max}(n)$ is reported using Mansfield et al.¹⁸ results as a full line and the present model as a dotted line (see text). The area below the limit corresponds to possible configurations whereas the area above R_v^{max} corresponds to impossible configurations. (A) Black dots are available analytical solutions for $n = 3, 4, 6, 8$, and 12 . The arrows display the schematic trace of a nucleation and growth experiment. In this graph, growth induces a horizontal motion (increase of V_{nuc}/V_{si} at constant N_{nuc}) and coalescence or expulsion induces a vertical motion (reduction of N_{nuc} at constant V_{nuc}/V_{si}). (B) Scenario S1 (mutual repulsion, $P_c = 0$), (C) scenario S2 (mutual repulsion, $P_c = 1$, $R_{vc} = 0$), and (D) scenario S3 (no mutual repulsion, $P_c = 1$, $R_{vc} = 0$). The circles correspond to $R_{si} = 42.5$ nm, and the square corresponds to $R_{si} = 27.5$ nm. The open, light gray and dark gray symbols correspond to a low ($h_c = 100$ nm and $R_{nuc} = 20$ nm), medium ($h_c = 100$ nm and $R_{nuc} = 15$ nm), and high ($h_c = 100$ nm and $R_{nuc} = 10$ nm) nucleation surface densities, respectively. The black dots in B–D correspond to results published by Désert et al.¹⁵ The images correspond to the simulated colloidal molecules.

impossible to obtain a colloidal molecule with more than three nuclei at the end.

With these general boundaries in mind, we explored the morphologies predicted by the model for several growth scenarios.

■ EXPLORATION OF THE MODEL LIMIT BEHAVIOR

We considered the production of colloidal molecules according to these simple model rules for three different scenarios. In scenario 1 (S1), we explored loosely attached nuclei that can easily move at the surface of the seed through mutual repulsion and tend to detach when the seed starts to be too crowded. In this case, no coalescence events are possible ($P_c = 0$), and all the attached and expelled nuclei have the same final size. In scenario 2 (S2), we investigated the same easily moving nuclei but with $P_c = 1$ and $R_{vc} = 0$. In this case, the number of attached nuclei decreases at the beginning of the reaction through coalescence events, then through expulsion when the monomer amount decreases. Thus the final colloidal molecules contain nuclei of various sizes and polydisperse expelled nuclei may be present. In scenario 3 (S3), we explored the situation where the nuclei are solidly attached to the seed surface. In this case, no mutual repulsion is possible, and the nuclei grow at their birth location. As the nuclei are randomly distributed on the surface of the sphere, several nuclei will touch each other and coalesce ($P_c = 1$, $R_{vc} = 0$) far before the maximum volume ratio for the given nuclei number is reached.

Figure 3B–D shows the evolution of a colloidal molecule morphology in the course of the growth process for the three scenarios. The plot relates the number of attached nuclei as a function of the volume ratio (or progress of the polymer conversion). Two seeds of $R_{si} = 27.5$ and 42.5 nm were considered with the three nucleation surface densities of Figure 1. For scenario S1 (Figure 3B), it is observed that the number of nuclei is constant in the first part of the growth. Indeed, as the nuclei can repel each other freely on the surface of the seed, the first collisions between the growing nuclei lead first to a rearrangement of the surface configuration of the nuclei. It is only when the volume ratio between the nuclei and the seed gets close to the maximum volume ratio $R_v^{max}(n)$ that this reorganization is no longer able to find a configuration allowing further growth. At this point, the number of nuclei starts to decrease. In this case, as $P_c = 0$, the decrease of the nuclei number occurs through detachments of nuclei from the surface. The volume of the detached nuclei is systematically taken into account in the computation of V_{nuc}/V_{si} . Therefore, the obtained results are above the $R_v^{max}(n)$ curve due to the contribution of the detached nuclei. The proportion of detached nuclei is known through the difference between the initial nuclei number and the nuclei number at each point of the growth. For example, at the end of the growth for $R_{si} = 42.5$ nm and high nucleation rate law, 86% of the initial nuclei have been detached from the surface ($28 - 4 = 24$ detached nuclei for $R_v = 1000$). The volume ratio of the four attached nuclei and silica would thus be $R_v = 4 \times (1000/28) = 142$ at the end of the simulation. This value is, as expected, well below $R_v^{max}(4)$ (see Supporting Information).

In Figure 3B, it is interesting to note that the nucleation stage is crucial in scenario S1. Indeed, the three nucleation surface densities do not give the same morphologies at a given value of V_{nuc}/V_{si} . The growth curves are parallel because of the different total number of growing polymer spheres. For the high nucleation surface density, many latex spheres grow, leading to

overall smaller nuclei for a given volume ratio. Therefore, the morphologies obtained in this case contain more attached nuclei and a significant proportion of free latex particles as compared to the low nucleation surface density where fewer attached nuclei are present with less free latex.

In the second scenario (S2), the nuclei can repel each other on the surface upon contact, but, in this case, they can coalesce with a probability P_c when no surface arrangements can sustain the nuclei growth. Therefore, the final nuclei do not have all the same size. Figure 3C shows an example of the nuclei growth according to this scenario as a function of the evolution of the volume ratio between the nuclei and the seed. During a growth according to S2, two stages can be noticed. In the first stage, before R_v reaches the maximum surface ratio $R_v^{\max}(n)$, the number of surface nuclei remains constant and equal to $4\pi R_{si}^2 \tau_{nuc}$. During this first stage, the nuclei mutually push each other to continue their growth. When R_v reaches $R_v^{\max}(n)$, surface coalescence events occur and reduce the number of surface nuclei. As $R_v^{\max}(n-1)$ is higher than $R_v^{\max}(n)$, growth is again possible. Therefore, throughout the second stage of the growth, the number of nuclei almost perfectly follows the critical $R_v^{\max}(n)$ line. It is interesting to note that some morphologies are obtained in the region slightly above $R_v^{\max}(n)$. Coalescence introduces a polydispersity in the size of the nuclei. It is obvious that polydispersity can help increasing the maximum volume ratio for a certain number of nuclei. Indeed, it is possible to fill the gaps between already touching spheres by using small enough new spheres. However, from Figure 3C, it is observed that the type of polydispersity produced in such growth process is not able to increase the volume ratio well above $R_v^{\max}(n)$.

Another interesting feature of the outcomes of scenario S2 is that, at high enough volume ratio, the obtained morphologies are independent from the nucleation rate. Indeed, whatever the nucleation surface density, the growth curve follows almost perfectly the maximum volume ratio limit. Therefore, the average number of nodules only depends on the volume ratio between the polymer and the silica seeds. This is, however, not the case of the polydispersity of the nodules. For example, in the case of the medium nucleation rate and $R_{si} = 27.5$ nm, at $R_v = 50$ the growth curve touches the $R_v^{\max}(n)$ limit for the first time. At this point, the six initial nuclei have all the same size, and no coalescence event has occurred yet. At the same value of R_v for the high nucleation surface density, the cluster also contains an average of six nuclei. However, they are the results of a number of coalescence events that have already created a polydispersity between the remaining nuclei. The time spent by the cluster on the $R_v^{\max}(n)$ limit is efficient in always selecting the same morphologies. However, this is at the expense of a polydispersity proportional to the difference between the initial and final number of nuclei.

The last scenario (S3) considers solidly attached surface nuclei. In this case, no mutual repulsion between the nuclei is possible, and collisions lead to coalescence. Figure 3D shows an example of a nucleation growth simulation for three surface nucleation surface densities. In the case of S3, the nuclei cannot move upon contact. As they are randomly distributed on the surface of the seed, nuclei collisions can occur from the very beginning of the growth, even if significant free space exists on the surface of the seed. Therefore, in this scenario, the number of attached nuclei starts to decrease from the beginning. In Figure 3D, it is thus observed that the number of nuclei lie below the $R_v^{\max}(n)$ curve and decrease in a similar trend. In the

image of the simulated colloidal molecules, it is observed that the surface nuclei are far from one another. Significant free space obviously exists on the surface. This is very different from S1 and S2, where much less free space exists on the surface due to the constant optimization of the surface arrangement through mutual repulsion of the nuclei. In the case of scenario S3, the importance of the nucleation rate is also to be noticed. As in the case of S1, the two growth curves are not following the same line. In other words, the resulting morphology at a given R_v is also a function of the nucleation surface density.

For a given scenario and given values of R_{si} and τ_{nuc} , the model predicts final morphologies for the volume ratio R_v . It is interesting to note that R_{si} is precisely known from the seed synthesis step. The maximum value of R_v is known from the introduced concentrations and densities of silica seeds C_s ($\text{g}\cdot\text{L}^{-1}$), ρ_s ($\text{g}\cdot\text{cm}^{-3}$), and monomers C_p ($\text{g}\cdot\text{L}^{-1}$), ρ_p ($\text{g}\cdot\text{cm}^{-3}$) ($R_v = \rho_p C_s / \rho_s C_p$). The only unknowns are the nuclei surface densities and the relevant growth scenario (S1, S2, or S3). As discussed earlier, the importance of τ_{nuc} is not the same for all growth scenarios. Indeed, for S1 and S3, it controls both the average nodules number and nodule polydispersity. For S2, it will only influence the nodule polydispersity if $R_v^{\max}(n)$ has been reached.

Finally, it appears that we cannot yet propose a model in which no free parameters exist. We still have to demonstrate the validity of the growth scenario and the validity of the nucleation surface density. We, however, set the basis of a rational model that could benefit from the comparison with experiments for further validations or improvements. In the following section, we will compare the predictions of the model with recently published results on the synthesis of hybrid polystyrene/silica colloidal molecules.

■ COMPARISON WITH EXPERIMENTAL RESULTS

In this section, we compare the outputs of the different growth scenarios and nucleation surface densities with experimental results of heterogeneous nucleation of polystyrene on monodisperse silica seeds. The surface of the silica seeds was previously modified by the use of MMS at a nominal surface density of $0.5 \text{ MMS}\cdot\text{nm}^{-2}$. A mixture of Synperonic NP30 and sodium dodecylsulfate (95/5 wt/wt) was used during the synthesis.¹⁵

Using such recipe, high yields of tetrapods or hexapods were obtained using silica seeds with a radius of 27.5 and 42.5 nm, respectively, for a constant styrene concentration of $100 \text{ g}\cdot\text{L}^{-1}$. The experimental R_v values (taking into account the partial conversion of styrene) were determined by weighting to be 54 and 36.4 for $R_{si} = 27.5$ and 42.5 nm, respectively. From the experimental conditions, all necessary parameters for the model are fixed. The only possible variations are the growth scenarios (S1, S2, S3, or maybe mixed scenarios) and the nucleation surface densities.

The first comparison that can be easily made with the model outputs is to compare the experimentally obtained dominant morphologies with the simulated morphologies predicted by the model for the different scenarios S1, S2, and S3 (see experimental points in Figure 3) for the wide range of nucleation surface densities presented in Figure 1.

From this comparison, it is first obvious that the scenario S3 is not able to predict the experimental results. Indeed, for scenario S3, the morphologies (hexapods, tetrapods) are always predicted to occur at much smaller R_v than the experimental results, whatever the assumed nucleation surface density. The

fact that the experimentally obtained hexapods are lying very close to the theoretical maximum limit $R_v^{\max}(n)$ is anyway a very strong evidence that the system is optimizing its organization to accommodate the maximum amount of polymer on the surface of the silica seeds. This is the case for scenarios S1 and S2 where the polymer nuclei can mutually repel each other while attached on the seed to optimize the surface occupancy. The suspected behavior of nuclei surface motion upon collision is thus supported by the model predictions.

For both scenarios S1 and S2, the experimental points lie in the plausible region for the nucleation surface density. In order to check whether a common nucleation surface density able to predict the experimentally observed proportions of morphologies exists, we systematically varied the value of R_{nuc} in the range 10–20 nm at a fixed experimental value of R_v (54 for $R_{\text{si}} = 27.5$ nm and 36.4 for $R_{\text{si}} = 42.5$ nm). The obtained proportions are shown in Figure 4.

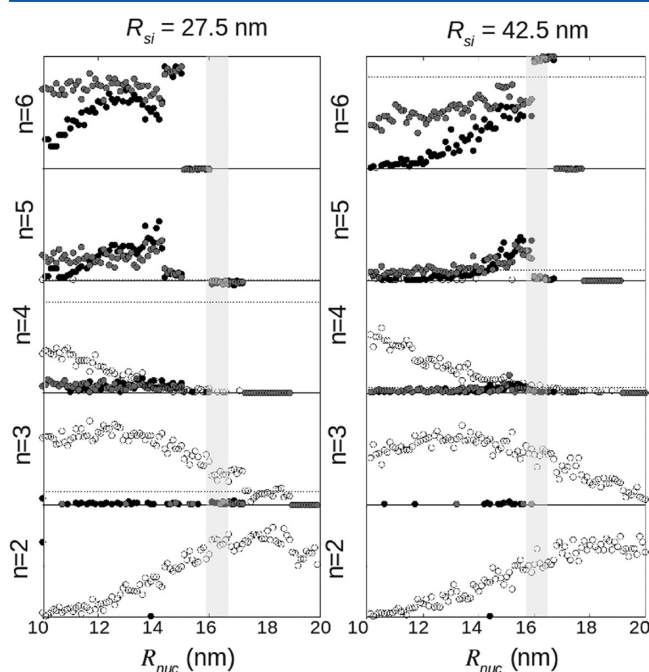


Figure 4. Proportion from 0% to 100% of morphologies (the points with 0% are not shown for clarity) as a function of R_{nuc} for two different seed radii $R_{\text{si}} = 27.5$ and 42.5 nm and imposed volume ratio R_v of 54 and 36.4, respectively, for scenarios S1 (black circles), S2 (gray circles) and S3 (open circles). The dotted lines correspond to the experimentally determined morphology proportions. The grayed area depicts the most suitable R_{nuc} common for the two scenario S1 and S2.

There exists for both seed sizes a common range of possible R_{nuc} values for which the predicted proportions are close to the experiments. This is especially true for $R_{\text{si}} = 42.5$ nm, where the predicted proportions are almost equal to the experimental ones. For $R_{\text{si}} = 27.5$ nm, the most favorable range of R_{nuc} predicts almost 100% of tetrapods. According to eq 1, the common parameters for the nucleation gives initial numbers of nuclei of 4 and 6 for $R_{\text{si}} = 27.5$ and 42.5 nm, respectively. This is not surprising for the case of the tetrapods, as in the case of scenario S1 and S2 the only possibility to get 4 nuclei far from the maximum limit $R_v^{\max}(4)$ is to have them from the beginning of the nucleation. The slightly less than 100% proportion of

final nuclei may come from the fact that a perfect homogeneity of the initial nuclei number, as considered in the model, is not likely experimentally. In the case of the hexapods, the proportions are modified by the fact that the experimental R_v is closer to $R_v^{\max}(6)$. Some selection processes by expulsion (S1) or coalescence (S2) start to create colloidal molecules with less than the 6 initial nuclei number. It is also interesting to note that, experimentally, no heptapod were observed for $R_{\text{si}} = 42.5$ nm and no pentapod for $R_{\text{si}} = 27.5$ nm, further confirming the probable initial nucleation of 4 and 6 nuclei, respectively.

In order to distinguish the differences between S1 and S2, it is necessary to go beyond the simple comparison of the proportion of population of final attached nuclei. It is also interesting to compare the predictions of the different scenarios and the experiments with respect to the size distribution of the attached nodules. Indeed, the scenario S1 predicts that nodules have exactly the same size among sometimes free latexes, whereas scenario S2 predicts some size polydispersity of the attached nodules.

It is obvious from Figure 5 that the nuclei can have different sizes and that the amount of free latex is very low. On the one hand, this observation is clearly in favor of the scenario S2, but, on the other hand, it is surprising for the case of the tetrapods, which are far from the maximum volume limit. In this case, no coalescence would occur in a scenario S2 where surface motion through mutual repulsion of nuclei would prevent coalescence until the limit is reached. Two possibilities could create such a polydispersity in the model. In the case of scenario S3, a very high nucleation rate could be imagined. It is, however, not likely for two main reasons. First, the same overall recipe should not allow surface motion for large seeds and not for small ones. Second, the very high nucleation rate required to have the right morphology in scenario S3 is not observed in the early stage experiments (see Figure 1 and the work of Reculosa et al.¹²).

The other possibility would be to imagine that the surface motion is not fully efficient. If a probability that the surface motion is blocked exists, then early coalescence could occur and lead to a slight polydispersity. Introducing a probability of 0.8% for each mutual repulsion event to be blocked, the morphology proportions are predicted to be almost the same as observed experimentally. A lower mutual repulsion blockage probability of 0.15% has to be applied to the hexapods case to reduce the hexapod proportion from 97% to the experimentally observe proportion of 80%. Figure 6 shows the proportions predicted by the model compared to the proportions published by Désert et al.¹⁵

The postulated difference between the mutual repulsion blockage probabilities as a function of the seed radius has currently no well-established origin, and could be correlated to differences in the curvature radii, the contact angles, and/or the surface roughness of the prepared seeds.

If the proposed model has captured the true mechanism, then it is impressive to see that the work of Désert et al.¹⁵ has really selected the optimal reaction pathway to obtain the purest colloidal molecules. Indeed, the optimal recipe is to have at the end of the nucleation step the desired number n of surface nuclei and to grow them almost up to the $R_v^{\max}(n)$ limit allowing the most efficient surface motion without nuclei detachment or coalescence. Any other reaction pathway would lead to less perfect morphologies because of selections through coalescence or detachment inducing a higher polydispersity or the presence of free latex particles, respectively.

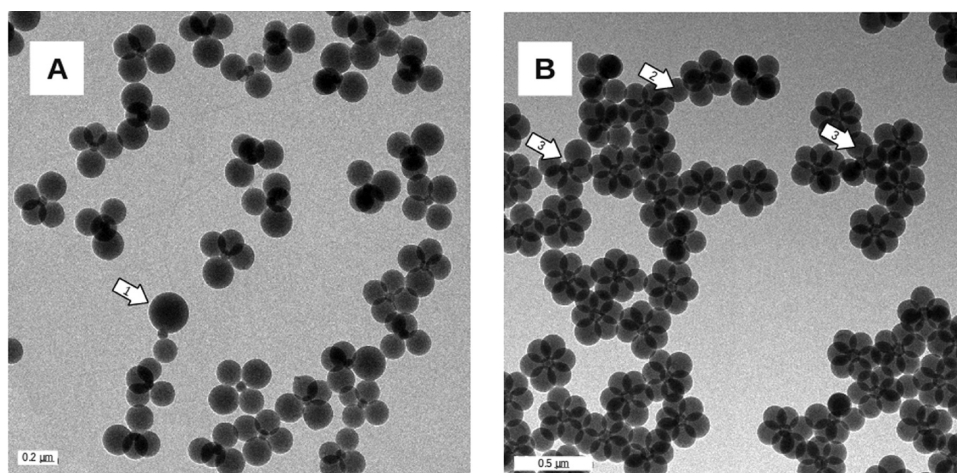


Figure 5. TEM images of experimental morphologies obtained for seeds of $R_{si} = 27.5$ nm (A) and $R_{si} = 42.5$ nm (B). The arrows indicate (1) a coalesced nucleus, (2) a free latex particle, and (3) pentapods.

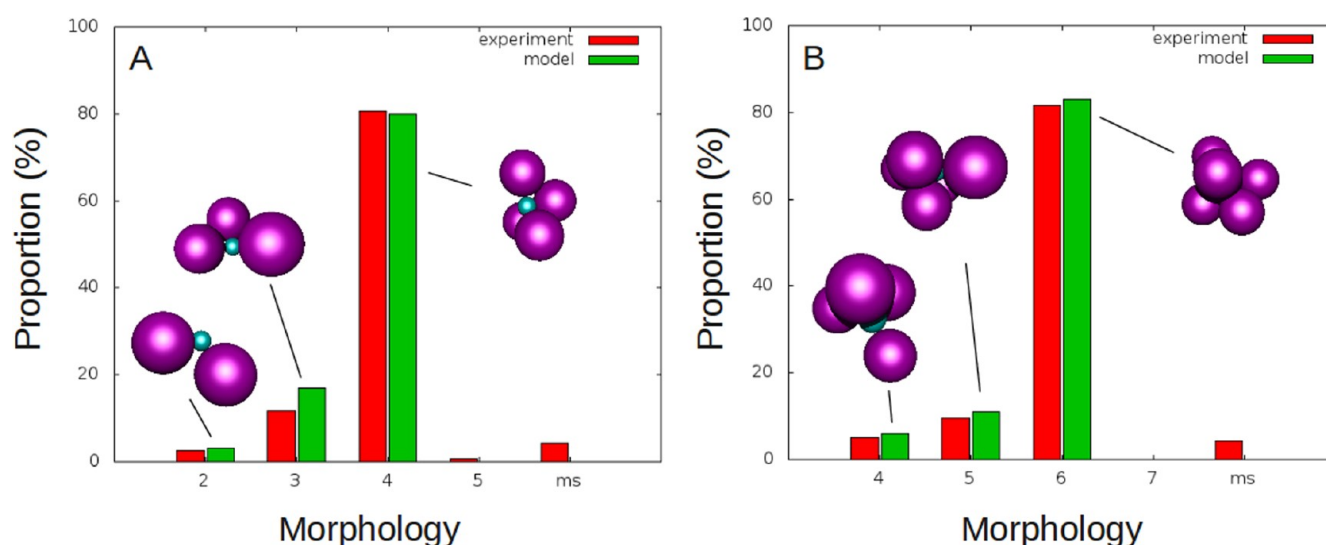


Figure 6. Morphology proportions for a scenario S2 with a nucleation radius of $R_{nuc} = 16.5$ nm at $R_v = 54$ and 36.4 for $R_{si} = 27.5$ and 42.5 nm, respectively, compared to the proportions published by Désert et al.¹⁵ A mutual repulsion blockage of 0.8 and 0.15% was introduced for $R_{si} = 27.5$ and 42.5 nm, respectively. The multisilica morphology (ms) is not considered in the present model.

Our very general model seems to be able to predict the obtained morphologies. However, it is based on several assumptions that have to be further verified or improved. For example, we supposed a 180° contact angle. Lower contact angle could significantly shift the boundary $R_v^{max}(n)$ to the left. It is known that this contact angle is a function of the MMS coverage, higher coverage being able to lead to the full encapsulation of the silica seed.^{12,13} We suppose that the nuclei are rigid. It would be possible, especially if the nuclei are liquid-like, that a certain degree of deformation exists. This would shift the boundary $R_v^{max}(n)$ to the right. However, more importantly, we suppose a single nucleation step and nucleation surface density. It is clear from the present results that the early reaction times (and more particularly the nucleation step) control for a large part the behavior of such systems. Any experimental results allowing the detailed exploration of the initial step would be of the utmost interest, especially to explore the coupling between the synthesis parameters (R_{si} , R_v) and the nuclei initial surface density.

CONCLUSION

The present model allows the prediction of morphologies obtained after a heterogeneous nucleation growth based on purely geometric rules. The only unknowns required by the model are the nucleation surface density and the growth scenarios (coalescence or expulsion, mutual repulsion or not). We show that there exists a maximum volume ratio $R_v^{max}(n)$ for each final nuclei number n that sets a boundary for any recipes intended to produce almost pure suspensions of a colloidal molecule containing n final nuclei.

Using comparisons between well-defined synthesis and the model predictions, we were able to determine the most probable growth scenario. In the case of the high yield production of hexapods, the observed optimal volume ratio is very close to the limit $R_v^{max}(6)$. Only growth scenarios allowing mutual repulsion of the nuclei at the surface of the seed are able to give such results. The fact that nuclei of different sizes are observed and that few free latex particles exist is in favor of the possible coalescence of the nuclei during their growth. The experimentally observed polydispersity of the tetrapods and

hexapods could be reproduced very well when a low probability of mutual repulsion blockage is considered. The model results clearly stress the need for a detailed investigation of the early reaction times.

■ ASSOCIATED CONTENT

■ Supporting Information

Explanation of the derivation of eq 1 and the values used for $R_v^{\max}(n)$ are presented as Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

■ Web-Enhanced Feature

Simulated colloidal molecules illustrating S1, S2, and S3 are available in the HTML version of the paper.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: antoine.thill@cea.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the TOCOMO project, Grant ANR-07-BLAN-0271, of the Agence Nationale pour la Recherche.

■ REFERENCES

- (1) Nelson, E. C.; Braun, P. V. Enhancing colloids through the surface. *Science* **2007**, *318*, 924–925.
- (2) Glotzer, S. C.; Solomon, M. J. Anisotropy of building blocks and their assembly into complex structures. *Nat. Mater.* **2007**, *6*, 557–562.
- (3) van Blaaderen, A. Materials science - Colloids get complex. *Nature* **2006**, *439*, 545–546.
- (4) Li, F.; Josephson, D. P.; Stein, A. Colloidal assembly: The road from particles to colloidal molecules and crystals. *Angew. Chem., Int. Ed.* **2011**, *50*, 360–388.
- (5) Sacanna, S.; Pine, D. J. Shape-anisotropic colloids: Building blocks for complex assemblies. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 96–105.
- (6) Duguet, E.; Désert, A.; Perro, A.; Ravaine, S. Design and elaboration of colloidal molecules: An overview. *Chem. Soc. Rev.* **2011**, *40*, 941–960.
- (7) Xu, D. Z.; Wang, M. Z.; Ge, X. W.; Lam, M. H. W.; Ge, X. P. Fabrication of raspberry SiO₂/polystyrene particles and super-hydrophobic particulate film with high adhesive force. *J. Mater. Chem.* **2012**, *22*, 5784–5791.
- (8) Perro, A.; Manoharan, V. N. Bulk synthesis of polymer-inorganic colloidal clusters. *Langmuir* **2010**, *26*, 18669–18675.
- (9) Daisuke, N.; Takuya, U.; Daisuke, O. K. Size control of polystyrene nodules formed on silica particles in soap-free emulsion polymerization with amphoteric initiator. *Colloid Polym. Sci.* **2009**, *287*, 1051–1056.
- (10) Weili, Q.; Yilong, W.; Ping, H.; Hong, X.; Hongchen, G.; Donglu, S. Synthesis of asymmetric inorganic/polymer nanocomposite particles via localized substrate surface modification and miniemulsion polymerization. *Langmuir* **2008**, *24*, 606–608.
- (11) Reculosa, S.; Poncet-Legrand, C.; Ravaine, S.; Mingotaud, C.; Duguet, E.; Bourgeat-Lami, E. Syntheses of raspberry-like silica/polystyrene materials. *Chem. Mater.* **2002**, *14*, 2354–2359.
- (12) Reculosa, S.; Mingotaud, C.; Bourgeat-Lami, E.; Duguet, E.; Ravaine, S. Synthesis of daisy-shaped and multipod-like silica/polystyrene nanocomposites. *Nano Lett.* **2004**, *4*, 1677–1682.
- (13) Reculosa, S.; Poncet-Legrand, C.; Perro, A.; Duguet, E.; Bourgeat-Lami, E.; Mingotaud, C.; Ravaine, S. Hybrid dissymmetrical colloidal particles. *Chem. Mater.* **2005**, *17*, 3338–3344.
- (14) Perro, A.; Duguet, E.; Lambert, O.; Taveau, J. C.; Bourgeat-Lami, E.; Ravaine, S. Chemical synthetic route towards “colloidal molecules”. *Angew. Chem., Int. Ed.* **2009**, *48*, 361–365.
- (15) Désert, A.; Chaduc, I.; Fouilloux, S.; Taveau, J. C.; Lambert, O.; Lansalot, M.; Bourgeat-Lami, E.; Thill, A.; Spalla, O.; Ravaine, S.; Duguet, E. High-yield preparation of polystyrene/silica clusters of controlled morphology. *Polym. Chem.* **2012**, *3*, 1130–1132.
- (16) Batty, R. A.; Gibbons, G. W.; Rychenkova, P.; Sutcliffe, P. M. Polyhedral scattering of fundamental monopoles. *J. Math. Phys.* **2003**, *44*, 3532–3542.
- (17) Taveau, J. C.; Nguyen, D.; Perro, A.; Ravaine, S.; Duguet, E.; Lambert, O. New insights into the nucleation and growth of PS nodules on silica nanoparticles by 3D cryo-electron tomography. *Soft Matter* **2008**, *4*, 311–315.
- (18) Mansfield, M. L.; Rakesh, L.; Tomalia, D. A. The random parking of spheres on spheres. *J. Chem. Phys.* **1996**, *105*, 3245–3249.