January 2010

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Nucleation Control In Size and Dispersity of Metallic Nanoparticles: The Prominent Role of Particle Aggregation

by

Vernal N. Richards

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in St. Louis in partial fulfillment of the requirements for the degree of Doctor of Philosophy

August 2010

Saint Louis, Missouri
ABSTRACT OF THE DISSERTATION

Nucleation Control In Size and Dispersity of Metallic Nanoparticles: The Prominent Role of Particle Aggregation

by

Vernal N. Richards

Doctor of Philosophy in Chemistry

Washington University in St Louis, 2010

Professor William E. Buhro, Chair

The aim of this project is to investigate the effect of aggregative nucleation and growth on the final size and dispersity in metallic nanoparticle systems. Aggregative nucleation functions are determined for the first time for three nanocrystal systems, namely gold (Au), silver (Ag) and bismuth (Bi). These nucleation functions give critical information that correlates closely with the size and dispersity of the nanocrystals synthesized.

The aggregative nucleation functions and growth kinetics of pre-synthesized Au nanoparticles as a function of tetra-octylammonium bromide \((n\text{-octyl}_4\text{NBr})\) is investigated. For each kinetic trial, the time dependence of the aggregative nucleation rate is extracted from the early-time nanocrystal size distributions (CSDs), and fitted by a Gaussian profile. The height of the profile is the maximum nucleation rate, \(\Gamma_{\text{max}}\), and the \(2\sigma\) width is the time window for nucleation, \(\Delta t_n\). These nucleation parameters control the final mean size and size distribution of the coarsened nanocrystals. The coarsening kinetics are influenced by tetraoctylammonium bromide concentration because the nanocrystals are partially electrostatically stabilized.
A mechanistic study of Ag-nanoparticle growth by reaction of \([(\text{PPh}_3)_2\text{Ag(O}_2\text{CC}_{13}\text{H}_{27})]\) and AIBN is reported. The half-life for precursor disappearance at 130.0 ± 0.1 °C under the reaction conditions is determined to be 3.65 ± 0.42 min, which defines the time scale for classical (LaMer) nucleation and growth to be within the first 15 min (4 half-lives). The nanoparticle-growth kinetics are separately determined by TEM monitoring and UV-visible spectroscopy. Fits to the kinetic data establish that the active-growth regime extends to 58 min, and that Ostwald ripening ensues shortly thereafter. Evidence for an aggregative nucleation and growth process is obtained. The quantitative data indicate that classical nucleation and growth, aggregative nucleation and growth, and Ostwald ripening occur in consecutive time regimes with little overlap, and that nanoparticle growth is dominated by the aggregative regime.

The kinetics and mechanism of Bi-nanocrystal growth from the precursor Bi[\text{N(SiMe}_3)_2]\_3 are determined at various Na[\text{N(SiMe}_3)_2]\ additive concentrations. The results establish that aggregative nucleation and growth processes dominate Bi-nanocrystal formation. The time dependence of the aggregative nucleation rate – the nucleation function – is determined over the range of Na[\text{N(SiMe}_3)_2]\_2 concentrations studied. The time width of aggregative nucleation (\(\Delta t_n\)) is shown to remain reasonably narrow, and to correlate with the final Bi-nanocrystal size distribution. The maximum aggregative nucleation rate (\(\Gamma_{\text{max}}\)) is shown to vary systematically with Na[\text{N(SiMe}_3)_2]\_2 concentration, producing a systematic variation in the final nanocrystal mean size. The Na[\text{N(SiMe}_3)_2]\ additive functions as both a nucleation-control agent and an Ostwald-ripening agent.
ACKNOWLEDGEMENTS

Words are inadequate to convey the heartfelt appreciation I have for my graduate school advisor, Professor William Buhro. His support during my tenure has made what looked like an insurmountable task possible.

I also owe a debt of gratitude to Professors Richard Loomis and Sophia Hayes, who have served on my committee since 2005. Thank you for your feedback after Committee and Group Meetings, and the encouragement you gave to steer me in the right direction. I also want to thank Professors Patrick Gibbons, Jacob Schaefer and Daniel Giammar who so willingly agreed to be a part of my committee for my final examination.

I am compelled to make mention of a number of persons who helped in the technical aspect of this study. A number of hours were spent doing Transmission Electron Microscopy (TEM), and I am grateful to Dr. Angang Dong who provided initial training, and also Drs. Kevin Croat and Tyrone Daulton for their technical assistance. Dr. Fudong Wang, an invaluable member of the Buhro research group, was also instrumental in the acquisition of high resolution TEM images. Dr. Jeff Kao was instrumental in the acquisition of NMR data, especially those done at lower temperatures and Brian Gau from Gross’ research group was instrumental in the Mass Spectrometry studies. Professor Nigam Rath at the University of Missouri St. Louis was responsible for determining the crystal structure of the precursor used in the Ag studies.

Dr. Shawn Shields deserves special mention, as her initial work on aggregative nucleation and growth formed the substratum from which this work could come. Au and Bi data collected by her were analysed and incorporated in this study leading to a more
comprehensive analysis. Her continued availability for consultation speaks of her selflessness to this endeavor.

Dr. Patricio La Rosa was also available for helpful consultations on aspects of fitting equations and statistical analysis.

Thanks to the past and current members of the Buhro and Loomis research groups. Their presence has made my tenure in the laboratory a pleasant experience. I also want to thank my friends, especially those from International Friends and Life Christian Church, who have provided a safe haven in St Louis. I am also grateful to my other friends scattered over the face of the earth who still remember me and would give the occasional call.

Special Jamaican “big up” to my family, for their strong support. I am blessed to have a mother, brothers and a sister who support me 110%. Although now deceased, I thank my father for always valuing education and ensuring that I did not quit school at age four.

Finally I want to thank my Lord and Savior Jesus Christ, who has showed me immeasurable favor during this sojourn.
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Introduction
This dissertation reports the aggregative nucleation and growth of gold (Chapter 1), silver (Chapter 2), and bismuth (chapter 3) nanoparticles. The mechanistic pathway for the evolution of near-monodisperse gold nanoparticles was undertaken from preformed Brust synthesized nanoparticles, whilst the studies of the evolution of near-monodisperse silver and bismuth nanoparticles were undertaken starting with molecular precursors. In the gold and bismuth studies, size and dispersity control were investigated as a function of varying the ionic strengths of the reaction media by the amount of organic salt additives. In the silver study aggregative nucleation and growth were studied by investigating the kinetics of precursor decomposition and comparing this timescale with that of nanoparticle growth.

Purposeful control over nanocrystal mean size and the routine production of narrow size distributions are two of the most important issues confronting nanocrystal syntheses. Whereas dispersity issues have been empirically resolved to a great extent, no general clear-cut means for achieving a predetermined size and narrow size distribution have yet emerged. The nonexistence of any such detail lies mainly in the fact that the mechanisms of nanocrystal growth are currently poorly understood in the synthetic community. Having a sound grasp on the mechanisms underlying nanocrystal growth would invariably lead to the development of improved synthetic methods that would correctly predict synthetic outcomes.

The LaMer mechanism\textsuperscript{1-3} which was originally developed to account for the growth of near-monodisperse micrometer-scale sulfur sols in aqueous dispersions is most commonly invoked\textsuperscript{4-9} as the mechanism of choice to account for nanocrystal nucleation and growth. Figure I-1 is an illustration of this classical mechanism\textsuperscript{10} and accounts for nucleation and growth in the following manner: In stage I, the monomer units that result from precursor decomposition increase in concentration and cause the solution to become supersaturated. At
a critical supersaturation in stage II, burst nucleation occurs which establishes the number of nuclei viable for growth. Viable nuclei are those that are thermodynamically stable to resist dissolution. Burst nucleation decreases the supersaturation of the system because monomer units are being consumed more rapidly than they are generated. This decrease in supersaturation prohibits the formation of additional nuclei and so nucleation is abated. In stage III, viable nuclei continue to grow by consuming the molecular-nutrient species made available from the continued decomposition of the precursor.

![LaMer plot showing the change in supersaturation as a function of time.](image)

**Figure 1-1.** LaMer plot showing the change in supersaturation as a function of time.¹⁰

Implicit in burst nucleation is the notion that all particles are nucleated in an early time interval. Similar growth histories then result as the nuclei grow competitively by near-equal division of the available nutrient. The result is crystals that are monodisperse at the end of the growth period. In principle, a knowledge of the number of nuclei formed in the nucleation window and the amount of nutrient available would allow prediction of the final
particle mean size. Therefore, if nanocrystals are grown by the LaMer mechanism, purposeful control over mean size and size distribution would require control over the classical nucleation process. However, several studies have established that many and perhaps most solution-based syntheses of near-monodisperse nano- and microparticles do not conform to the LaMer mechanism.\textsuperscript{11-32}

Another well-invoked mechanism used to account for growth is Ostwald ripening\textsuperscript{33-39} This mechanism has found widespread application in cases where growth occurs in the absence of molecular precursors and thus a constant supply of monomer units. Consequently growth by Ostwald ripening has been referred to as self focusing.\textsuperscript{33} To account for growth using the Ostwald ripening mechanism, consider two different sized particles in solution, as illustrated in Figure I-2. These particles are in equilibrium with their immediate solution environment. Because of its larger surface free energy brought about by its larger surface-area-to-volume ratio, the small particle will experience a faster rate of dissolution than deposition of monomer species. In order to maintain their respective equilibria, monomers dissolved from the small particle will diffuse from that environment and enter the vicinity of the large particle. In order to restore its equilibrium, the large particle will experience an increased rate of monomer deposition. This leads to an increase in size of the large particle and a continued diminishing in size of the small particle. Ostwald ripening has been presented as the operative mechanism responsible for size increases in Au and other noble-metal nanocrystals when small nanocrystals have been used as the starting material.\textsuperscript{34-39} The kinetic growth profile is quite distinct as shown in Figure I-3. The absence of an induction period distinguishes this mechanism from those mechanisms that require a build up of nuclei for growth to proceed.
Figure I-2. Schematic diagram of Ostwald ripening illustrating the dissolution of the smaller particle and reprecipitation of dissolved monomer units on the larger particle. The large monomer environment around the small particle is caused by its higher solubility.

Figure I-3. Kinetic profile of Ostwald ripening growth mechanism. $\bar{V}(t)$ is the mean nanocrystal volume at time $t$. $\bar{V}(t)$ does not start at zero because a size distribution of particles is initially present.

The principal deficiency in the LaMer and Ostwald-ripening mechanisms is that particle aggregation, which has been shown to participate in the growth processes in many cases, is unaccounted for. Evidence for aggregative growth includes direct observation of particles composed of smaller primary nanocrystals,\textsuperscript{17,19,25,29-32} decreasing particle number
densities with time,\textsuperscript{22,23,27,40} kinetic studies\textsuperscript{12-16} and the time evolution of (nano)crystal size distributions (CSDs),\textsuperscript{19-23,27,28} and theoretical results establishing that small nanocrystals are colloidally unstable and aggregate on time scales faster than classical growth.\textsuperscript{27} Furthermore, Alivisatos and coworkers recently reported videos of aggregative growth recorded in TEM studies.\textsuperscript{9} Indeed, a reexamination of the growth of LaMer sulfur sols established that the particle number density goes through a maximum after the nucleation period has ended,\textsuperscript{40} strongly implicating the participation of aggregative processes even in this archetypal case.\textsuperscript{40-42}

Aggregative nanocrystal growth is now becoming well recognized in the mechanistic community. The contributions of Alivisatos,\textsuperscript{9} Banfield,\textsuperscript{30-32} Finke,\textsuperscript{12-16} Matijević,\textsuperscript{17-20} Penn,\textsuperscript{24,29-31} Privman,\textsuperscript{19-21} Tsapatsis,\textsuperscript{22,23} Turkevich,\textsuperscript{25} and Zukoski\textsuperscript{26-28} have paved the way for this mechanism to be seriously consider as a viable mechanistic option for the formation of monodisperse particles. Additionally, colloidal crystallization, which is inherently an aggregative process, is now commonly used in the mechanistic community as a model for classical nucleation and growth.\textsuperscript{43-45}

When aggregative processes dominate nanoparticle growth, by definition the classical nucleation and growth that precede aggregation are rapid and not rate determining. The number of viable, growing particles is established during the assembly of critical-sized aggregates of smaller, or primary, nanocrystallites (see Figure I-4).\textsuperscript{18,20,21,26,27} This process may be considered a second nucleation step – a nonclassical, aggregative nucleation step.\textsuperscript{18,20-22,26,46} The critical aggregates so assembled may remain as aggregates,\textsuperscript{17,19,25} or coalesce to single or polycrystalline particles.\textsuperscript{14,24,25,29-32,47,48} Growth is subsequently accomplished by addition of primary nanocrystallites to the critical aggregates,\textsuperscript{18-21,26,27} and
then to the resulting supercritical nanoparticles, until all primary nanocrystallites are consumed and active growth ceases (see Figure I-4). The description given here for aggregative nucleation and growth closely resembles that for classical nucleation and growth. In fact both processes are analogous, the prime difference being primary nanoparticles replace molecular monomers as the nutrient species. As was discussed with the classical mechanism, control over nanoparticle size and dispersity may also be achieved by controlling the nonclassical, aggregative-nucleation process. Whereas nucleation and growth have been re-defined in this mechanism, Ostwald ripening, if it occurs, maintains its original meaning. Thus the dissolution of monomer species is not the loss of primary particles but as was described above, molecular species.

![Figure I-4. Schematic diagram of three stages of nanocrystal growth – nucleation, growth, and Ostwald ripening – and the commonly observed sigmoidal kinetic profile. $\bar{V}(t)$ is the mean nanocrystal volume at time $t$.](image)

The classical, LaMer model for nucleation in a closed system (that is, having a fixed amount of precursor) features an initially increasing nucleation rate as nutrient concentration increases and critical nuclei are assembled, which rises to a maximum and subsequently falls
off as supersaturation and therefore the driving force for nucleation is relieved\textsuperscript{1-3} (see Figure I-1, stage II). We will refer to this time-dependent nucleation rate as the nucleation function.

In the absence of aggregation, the width of the classical nucleation function, or the time window for nucleation, determines the final size distribution. In the absence of aggregation, the integrated area under the classical nucleation function determines the number of growing particles, and therefore, along with the quantity of nutrient present determines the final average particle size. We will show here, as others have shown previously, that the nucleation function for nonclassical, aggregative nucleation exhibits the same general features.\textsuperscript{50,51}

The very short spatial and time scales have precluded direct observation of a classical nucleation process. However, the longer spatial and time scales associated with colloidal\textsuperscript{43} and protein\textsuperscript{52} crystallization have recently allowed the sizes of critical aggregates (aggregative nuclei) to be directly measured. Indeed, it is the increased length and time scales that make colloidal crystallization a good model for classical nucleation and growth.\textsuperscript{43-45} Complete nucleation functions have been experimentally determined in a few such cases.\textsuperscript{50,51} Figure I-5 replots experimental nucleation functions for the colloidal crystallization of charged copolymer spheres reported by Wette and coworkers.\textsuperscript{51} These nucleation functions were constructed from video data collected from an optical microscope. It should be noted that the aggregative nucleation rate rises to a maximum and then falls off in time in a manner analogous to that predicted by the classical LaMer model. Similarly, the comparatively large dimensions (~ 2 nm) of the primary Au, Ag and Bi nanocrystallites studied here allow us to experimentally measure the critical aggregate size and to obtain the aggregative-nucleation function from the early-time CSDs collected in growth experiments.
Figure I-5. Nucleation functions reported by Wette and coworkers\textsuperscript{51} for the crystallization of charged colloidal polymer spheres at three particle number densities listed in the inset legend. Gaussian fits to the nucleation-rate data are also plotted. Adapted with permission from [Wette, P.; Schöpe, H. J.; Palberg, T. J. Chem. Phys., 123, 174902.] Copyright [2005], American Institute of Physics.

Kinetic growth profiles of the nanoparticle systems studied here have been fit with a Kolmogorov-Johnson-Mehl-Avrami or KJMA equation.\textsuperscript{53-55} KJMA equations provide simple models used to describe the kinetics of classical nucleation and growth and certain solid-state phase transformations.\textsuperscript{56-58} KJMA analyses have also been applied to solution-based or melt crystallization of zeolites,\textsuperscript{59} lipids,\textsuperscript{60-62} polymers,\textsuperscript{63,64} β-haematin,\textsuperscript{65} and colloidal crystals,\textsuperscript{51} and to nanocrystal growth.\textsuperscript{66}

The KJMA equations used for the fittings in these studies are of the general form shown in equation 1, with slight modifications as will be shown in chapters 2 and 3.

\[
\tilde{V}(t) = 1 - \exp \left[ - (kt)^n \right] \quad (1)
\]
$\overline{V}(t)$ is the time dependent average increase in volume, $k$ is a rate parameter that convolves both nucleation and growth, and the exponent $n$ is related to the nucleation mechanism and dimensionality of growth. The convolution of nucleation and growth in $k$, along with the obscurity surrounding the actual meaning of $n$, are the two main criticisms leveled against the use of this equation to fit nanocrystal growth kinetics. However in these studies, $k$ is seen as a rate parameter and not a rate constant. To be used as a rate constant, $k$ would have to be determined from balanced equations. Its use as a rate parameter in these studies is primarily assigned to growth process and interpreted as the relative aggregative growth rates. We will show in Chapter 1 that $k$ is largely independent of the nucleation kinetics. Similarly, no attempt is been made to clarify the meaning of $n$, as its optimal values only serve to enhance the fits. Figure I-4 shows the characteristic S-shaped or sigmoidal-shaped curve for an aggregative nucleation and growth process. We will show that such data are well fit by KJMA models.

The aggregative model that is being proposed in this work, although useful and groundbreaking, is an oversimplification of the aggregative growth mechanism. For aggregation and coalescence to occur, dissociation, rearrangement and re-adsorption of the ligands at the particle surfaces are vital steps. The enthalpic and entropic changes that accompany these processes have not been explicitly considered in the mechanistic study being presented herein. We therefore recognize that further exploration of these thermodynamic changes is a necessary requirement to present a more comprehensive picture of the aggregative nucleation and growth mechanism.

Chapter 1 shows the determination of the aggregative nucleation functions for Au nanocrystals as a function of varying tetra-$n$-octylammonium bromide ($n$-octyl4NBr, TOABr)
concentrations. Information obtained from these functions correlates closely with the final sizes and size distributions. The role played by the TOABr in influencing the nucleation event is discussed. In Chapter 2, a mechanistic study of Ag-nanoparticle growth by reaction of \([\text{PPh}_3\text{Ag(O}_2\text{CCCl}_3\text{H}_2\text{)}]\) and AIBN is reported. Along with the determined nucleation function, the entire reaction pathway including the reaction mechanism is presented. The timescale for precursor disappearance and its relation to nanocrystal growth is examined in relation to the different nucleation and growth mechanisms. Chapter 3 reports on the aggregative nucleation functions and growth kinetics of Bi nanoparticles as a function of varying concentrations of the additive Na[N(SiMe₃)₂]. Final nanocrystal sizes and distributions are also correlated with the concentration of the Na[N(SiMe₃)₂], and the different roles that this salt can have on the growth system are discussed.
References

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Chapter 1

Nucleation Control of Size and Dispersity in Aggregative Nanoparticle Growth. A Study of the Coarsening Kinetics of Thiolate-Capped Gold Nanocrystals
Introduction

Gold is one of the most extensively studied noble metals in the nanocrystal community. Such extensive study is justified based on the wide range of applications of this particular metal in the nano-domain. Applications include medicine,\(^1\) biotechnology,\(^2\) catalysis\(^3\) and optoelectronics.\(^4\) These applications require specific sizes and narrow dispersity, thus successful synthetic methods should yield the aforementioned properties on a consistent basis. Reduction of gold salts in the presence of appropriate ligands such as alkanethiols \(^5,6\) and citrates \(^7-9\) has largely been responsible for the attainment of size and dispersity control. It is this size and dispersity control that makes Au a good model system to probe nucleation and growth mechanisms.

Although monodispersity in nanocrystal synthesis has been achieved to some degree, gaining a detailed understanding of the formation mechanism which invariably involves nucleation as well as growth is still elusive. This lack of understanding may be primarily attributed to the timescale of nanoparticle nucleation, and the high surface to volume ratio of small nanocrystal seeds.\(^10\) This high surface to volume ratio renders small nanocrystal seeds very unstable and thus their isolation and study difficult.\(^10,11\) The possibility of manipulating the nucleation function, that is, the maximum nucleation rate and the time window for nucleation, would invariably lead to a more direct approach in size and dispersity control. In the LaMer or classical nucleation process, the very short spatial and time scales coupled with the small sizes and instability of crystal embryos, have precluded even the observation of this function. Inability to observe also limits the possibility of manipulation. In the event that another nucleation process exists that has longer spatial and time scales, it is possible to envisage manipulation.
Studying Au formation and growth via citrate reduction, Kimling and coworkers\textsuperscript{12} proposed a multistep mechanism that involves complete reduction of the Au(III) to Au(0), followed by cluster formation by aggregation. Kraehnert and coworkers\textsuperscript{13,14} have studied the classical citrate and borohydride reductions and have proposed aggregative mechanisms in both cases. These are in contrast to the thermal ripening studies carried out on Au and other noble metal nanocrystals by Peng,\textsuperscript{15-17} and Stucky,\textsuperscript{18} who have ascribed growth to Ostwald ripening.\textsuperscript{19,20} Klabunde\textsuperscript{21,22} has invoked inverse Ostwald Ripening to account for the narrowing of size distributions seen in his studies. Whereas mechanisms have been invoked to account for the increase in sizes and narrowing of size distributions, no detailed accounts have been given to indicate that the nucleation process has a direct bearing on the size and monodispersity.

The coarsening of decanethiolate-capped Au nanocrystals in the presence of tetra-\textit{n}-octylammonium bromide (\textit{n}-octyl\textsubscript{4}NBr, TOABr) originally reported by Zhong and coworkers\textsuperscript{23,24} motivated this study. In his studies, aggregation and coalescence of small nanoparticles were proposed to be responsible for size evolution and narrowing of the size distribution. Zhong looked at parameters such as temperature, alkanethiolate chain length and Au concentration. His studies show that size evolution would not occur in the absence of TOABr irrespective of other parameter changes. This prompted us to investigate the role or roles played by TOABr in the size-evolution process.

The comparatively large dimensions (1.68 ± 0.36 nm) of the Brust-synthesized primary Au nanocrystallites used as the starting material in this study, allowed us to experimentally measure the crystal size distributions (CSDs) from the onset of investigation while varying the amount of TOABr. CSDs were used as a means to determine a critical-aggregate size,
from which the aggregative-nucleation functions were constructed. (We will present full
details of this in the results and discussion section.) From these functions the maximum
aggregative-nucleation rate and the width of the time window for aggregative nucleation
were extracted. The coarsening kinetics were studied here as a function of the TOABr
concentration, therefore we were able to observe the effect that this additive has on the
nucleation function. The time window for aggregative nucleation was found to vary
smoothly with TOABr concentration, and to correlate with the final nanoparticle size and
size distribution. The results confirm that aggregative growth may in this case be
electrostatically manipulated, and establish the synthetic utility of achieving control over the
aggregative-nucleation process. We will argue that these nucleation parameters are the
important control factors for aggregative-nanoparticle growth.

We provide evidence that excludes Ostwald ripening as the primary growth mechanism
during the active growth period, including the observation of polycrystalline particles and
early time bimodal size distributions, which are inconsistent with Ostwald ripening. The
growth rates were extracted from a KJMA model that fit well the kinetic (nanoparticle mean
size vs. time) data. The sigmoidal growth kinetics observed are also inconsistent with
equilibrium Ostwald ripening.\textsuperscript{25,26} Finally, close correlation of the extracted nucleation
parameters with the final mean sizes and size distributions also argue against Ostwald
ripening as the primary growth mechanism. The results reported here underscore the
importance of considering aggregative growth as a viable mechanism, in addition to Ostwald
ripening, for the coarsening of small nanocrystals.

The primary contribution of this study is the first quantitative experimental method for
determining the nucleation function – the time width and maximum rate of nucleation – for
the aggregative growth of nanocrystals. Significantly, the nucleation parameters are demonstrated to correlate strongly with the nanocrystal final mean size and size distribution. This approach may lead to powerful new methods for rational size control in nanocrystal synthesis. A table of abbreviations used in this chapter along with their definitions is provided below.

**Table 1-1.** List of abbreviations and their definitions.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSD</td>
<td>Nanocrystal size distribution</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>Nucleation rate (in s(^{-1}))</td>
</tr>
<tr>
<td>( \Gamma_{\text{max}} )</td>
<td>Maximum nucleation rate (in s(^{-1}))</td>
</tr>
<tr>
<td>( \Delta t_n )</td>
<td>Time window for nucleation (in min)</td>
</tr>
<tr>
<td>( \tau_n )</td>
<td>Time at which ( \Gamma_{\text{max}} ) is achieved (in min)</td>
</tr>
<tr>
<td>( V_{\text{crit}} )</td>
<td>Volume of the critical aggregate (in nm(^3))</td>
</tr>
<tr>
<td>( F_{\text{crit}} )</td>
<td>Fraction of the aggregates in the CSD having the critical volume</td>
</tr>
<tr>
<td>( \bar{V}(t) )</td>
<td>Nanocrystal mean volume at time ( t ) (in nm(^3))</td>
</tr>
<tr>
<td>( \bar{V}_{\text{lim}} )</td>
<td>Final mean nanocrystal volume (in nm(^3)), at the end of the active-growth regime</td>
</tr>
<tr>
<td>( k_g )</td>
<td>Growth rate (in s(^{-1}))</td>
</tr>
<tr>
<td>( n )</td>
<td>Avrami exponent (unitless)</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Determination of the nucleation function.** In this study, we obtained nucleation functions comparable in shape to those of Wette and coworkers\(^{27}\) in Figure I-5. Following the suggestion of Gualtieri\(^{28}\) we show that Gaussian fits to these curves (Figure I-5) provide reasonable approximations of their shapes. Because our nucleation-rate data were extracted from CSDs determined from TEM images, they are less extensive than Wette’s.\(^{27}\) Consequently, we employed Gaussian approximations rather than extensively determined nucleation functions in this work.
Studies of particle growth, including by aggregative processes, have established that the CSDs follow a characteristic time evolution, as diagrammed in Figure 1-1,11,29-37 with a peak emerging at the critical size. Initially, the CSD typically has an asymptotic shape. Subsequently, a peak emerges in the early-time CSDs,11,32,34-37 which then shifts to progressively larger size. The emergence of the peak results from a burst of nucleation,33 as the nucleation rate increases rapidly.32 In aggregative growth, this event is the formation of critical aggregates, which is an aggregative-nucleation process. Consequently, the peak first appears at the critical-aggregate size.33 Knowledge of the critical-aggregate size allows extraction of the nucleation function from the early-time CSDs, as described below.

**Figure 1-1.** Schematic diagram of the characteristic time evolution of the CSD in particle growth. CSDs are plotted as the fraction of nanoparticles of a given volume ($F$) vs. nanoparticle volume. Volume refers to the volume of individual nanoparticles. The time points $t_1$, $t_2$, and $t_3$ refer to starting, early, and later times, respectively. The CSDs are shown to evolve from asymptotic at $t_1$, to bimodal at $t_2$, and to unimodal at $t_3$ (and later times).

In this study, the conditions for the thermal coarsening of thiolate-capped Au nanocrystals closely approximated those reported in the original studies by Zhong and coworkers.23,24 The kinetics were determined as a function of TOABr concentration (see the
Experimental section). The starting nanocrystals, prepared by the Brust synthesis,\(^5\) had a mean diameter of 1.68 nm with a standard deviation in the diameter distribution of 0.36 nm, as determined by TEM (Figure 1-2a). Hereafter, these initially prepared Au nanocrystals are referred to as primary nanocrystals. For each kinetic trial, CSDs were measured by TEM at time intervals. In these trials, the aggregated Au nanocrystals readily coalesced, such that roughly spherical nanoparticles, rather than tight aggregates of nanoparticles, dominated the TEM images (Figure 1-2b). Some aggregates of primary nanoparticles were found. More significantly, polycrystalline nanoparticles were imaged by HRTEM at early times, prior to their coalescence into single nanocrystals (see below).

![Figure 1-2](image.png)

**Figure 1-2.** Representative TEM images of decanethiolate-capped Au nanocrystals. The quantity following the ± symbol is one standard deviation in the diameter distribution, expressed as a percentage of the mean diameter. (a) primary nanocrystals having a mean diameter \(d = 1.68 \text{ nm} \pm 21\%\); (b) nanocrystals thermally coarsened with [TOABr] = 0.362 M, having a mean diameter \(d = 5.37 \text{ nm} \pm 7.1\%\).

Diameter distributions were measured from the TEM images and converted to volume distributions by assuming spherical morphologies. The volume data so obtained were binned using the minimum bin width that avoided excessive noise or discontinuities in the resulting
CSDs. A constant bin width was used to construct the early-time CSDs, through the emergence of a peak at the critical volume. Figure 1-3 plots the early-time CSDs from one such trial with a TOABr concentration of 0.145 M. A peak first emerged (30 min) at a nanoparticle volume of $21 \pm 3 \text{ nm}^3$ (bin width = 6 nm$^3$), which is the volume of the critical aggregate, $V_{\text{crit}}$. This critical volume corresponds to $8.5 \pm 1.3$ mean primary nanocrystals. The $V_{\text{crit}}$ values so measured were not highly sensitive to bin width; the values determined over a range of bin widths were within the experimental error. The CSDs in Figure 1-3 may be compared to the idealized CSDs in Figure 1-1. The CSDs for subsequent trials are presented in Figures 1-4 to 1-9. $V_{\text{crit}}$ values for the other kinetics trials are in presented in Table 2.

**Figure 1-3.** CSDs for the coarsening trial conducted with [TOABr] = 0.145 M, at the times indicated in the inset legend. The data were binned using a bin size of 6 nm$^3$ for all CSDs. A peak is evident at $V_{\text{crit}} = 21 \text{ nm}^3$ in the CSDs at 30 and 45 min. CSDs are plotted as the fraction of nanoparticles of a given volume ($F$) vs. nanoparticle volume. Volume refers to the volume of individual nanoparticles.
Figure 1-4. CSDs for the coarsening trial conducted with [TOABr] = 0.264 M, at the times indicated in the inset legend. The data were binned using a bin size of 6 nm$^3$. A peak is evident at $V_{\text{crit}} = 21$ nm$^3$ in the CSDs at 30 min.

Figure 1-5. CSDs for the coarsening trial conducted with [TOABr] = 0.362 M, at the times indicated in the inset legend. The data were binned using a bin size of 6 nm$^3$ for the CSDs at 0-60 min, and 8 nm$^3$ for 90 to 150 min. A peak is evident at $V_{\text{crit}} = 15$ nm$^3$ in the CSDs at 15 min.
Figure 1-6. CSDs for the coarsening trial conducted with [TOABr] = 0.446 M, at the times indicated in the inset legend. The data were binned using a bin size of 6 nm$^3$ for the CSDs at 0-40 min, and 8 nm$^3$ for 50 to 90 min. A peak is evident at $V_{crit} = 21$ nm$^3$ in the CSDs at 15, 20 and 25 min.

Figure 1-7. CSDs for the coarsening trial conducted with [TOABr] = 0.579 M, at the times indicated in the inset legend. The data were binned using a bin size of 6 nm$^3$ for the CSDs at 0-35 min, and 8 nm$^3$ for 50 to 90 min. A peak is evident at $V_{crit} = 21$ nm$^3$ in the CSDs at 15 min.
Figure 1-8. CSDs for the coarsening trial conducted with [TOABr] = 0.634 M, at the times indicated in the inset legend. The data were binned using a bin size of 6 nm\(^3\) for the CSDs at 0-25 min, and 8 nm\(^3\) for 32 to 150 min. A peak is evident at \(V_{\text{crit}} = 15\) nm\(^3\) in the CSDs at 11 and 15 min.

Figure 1-9. CSDs for the coarsening trial conducted with [TOABr] = 0.681 M, at the times indicated in the inset legend. The data were binned using a bin size of 6 nm\(^3\) for the CSDs at 0-25 min, and 8 nm\(^3\) for 30 to 140 min. A peak is evident at \(V_{\text{crit}} = 15\) nm\(^3\) in the CSDs at 5 min.
Table 1-2. Table showing $V_{\text{crit}}$ values in nm$^3$ and number of mean nanocrystals for thermal coarsening at various [TOABr].

<table>
<thead>
<tr>
<th>[TOABr] (mol/L)</th>
<th>$V_{\text{crit}}$ nm$^3$</th>
<th>$N_{\text{crit}}$ (mean primary nanocrystals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.145</td>
<td>21 ± 3</td>
<td>8.5 ± 1.3</td>
</tr>
<tr>
<td>0.264</td>
<td>21 ± 3</td>
<td>8.5 ± 1.3</td>
</tr>
<tr>
<td>0.362</td>
<td>15 ± 3</td>
<td>6.0 ± 1.8</td>
</tr>
<tr>
<td>0.446</td>
<td>21 ± 3</td>
<td>8.5 ± 1.3</td>
</tr>
<tr>
<td>0.579</td>
<td>21 ± 3</td>
<td>8.5 ± 1.3</td>
</tr>
<tr>
<td>0.634</td>
<td>15 ± 3</td>
<td>6.0 ± 1.8</td>
</tr>
<tr>
<td>0.681</td>
<td>15 ± 3</td>
<td>6.0 ± 1.8</td>
</tr>
</tbody>
</table>

The proportion of aggregates in the CSD having the critical size or volume rises and falls with the aggregative-nucleation rate, $\Gamma$. Consequently, the fraction $F_{\text{crit}}$ of the aggregates in the CSD having the critical volume $V_{\text{crit}}$ is proportional to $\Gamma$, and hence the time dependence of $F_{\text{crit}}$ is proportional to the nucleation function, $\Gamma$ vs. $t$. Therefore, $F_{\text{crit}}$ was determined for each CSD as the nanoparticle count inside the bin containing $V_{\text{crit}}$ divided by the total nanoparticle count. The results extracted from the CSDs in Figure 1-3 are plotted as a function of time in Figure 1-10, along with a Gaussian fit to the data. Figure 1-10 constitutes an experimental curve that is proportional to the nucleation function for this trial ([TOABr] = 0.145 M).
Figure 1-10. Nucleation function and Gaussian fit for the coarsening trial conducted with [TOABr] = 0.145 M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively (see text).

The maximum aggregative nucleation rate $\Gamma_{\text{max}}$ was determined and the nucleation function (Figure 1-10) scaled as $\Gamma(t)$ by the following procedure. The total number $N$ of aggregative nuclei formed was calculated by dividing the total volume of Au used by the final mean nanocrystal volume (Table 3-1). The height $h$ of a Gaussian curve is related to its area $A$ and width $2\sigma$ according to eq 1. For the nucleation function, the area is equal to $N$, the width to $\Delta t_n$ (the $2\sigma$ breadth of the time window for nucleation), and the height to $\Gamma_{\text{max}}$ (eq 2). In this case $N = (4.57 \pm 0.51) \times 10^{16}$ and $\Gamma_{\text{max}} = (2.01 \pm 0.24) \times 10^{13} \text{ s}^{-1}$. (The reader will note that $\Gamma_{\text{max}}$ and $\Gamma(t)$ in general are rates not rate constants; they report the number of critical aggregates formed per second at a given time, within the entire experiment. Because the number of critical aggregates is unitless, the units on $\Gamma_{\text{max}}$ and $\Gamma(t)$ are $\text{s}^{-1}$.) Accordingly,
the function was rescaled by the right-hand vertical axis in Figure 1-10. Nucleation functions were similarly obtained for the kinetics for the range of TOABr concentrations used. The results are plotted in Figures 1-11 to 1-16. Table 1-3 lists all the $N$, $\Gamma_{\text{max}}$, and $\Delta t_n$ values.

\[
h = \frac{A}{2\sigma \sqrt{\frac{\pi}{2}}}
\]

(1)

\[
\Gamma_{\text{max}} = \frac{N}{\Delta t_n \sqrt{\frac{\pi}{2}}}
\]

(2)

**Figure 1-11.** Nucleation function and Gaussian fit for the coarsening trial conducted with [TOABr] = 0.264 M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively.
Figure 1-12. Nucleation function and Gaussian fit for the coarsening trial conducted with [TOABr] = 0.362 M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively.

Figure 1-13. Nucleation function and Gaussian fit for the coarsening trial conducted with [TOABr] = 0.446 M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively.
Figure 1-14. Nucleation function and Gaussian fit for the coarsening trial conducted with $[\text{TOABr}] = 0.579$ M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively.

Figure 1-15. Nucleation function and Gaussian fit for the coarsening trial conducted with $[\text{TOABr}] = 0.634$ M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively.
**Figure 1-16.** Nucleation function and Gaussian fit for the coarsening trial conducted with [TOABr] = 0.681 M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively.

**Table 1-3.** The aggregative nucleation and growth parameters extracted from the kinetic data for Au-nanoparticle coarsening as a function of TOABr concentration.

<table>
<thead>
<tr>
<th>[TOABr] (M)</th>
<th>$\tau_n$ (min)$^{a}$</th>
<th>$\Delta t_n$ (min)$^{b}$</th>
<th>$N$ $(\times 10^{16})^c$</th>
<th>$\Gamma_{\text{max}}$ $(\times 10^{13} \text{ S}^{-1})^d$</th>
<th>$k_g$ $(\times 10^{5} \text{ S}^{-1})^e$</th>
<th>$n^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.145</td>
<td>37.93 ± 0.86</td>
<td>30.19 ± 1.15</td>
<td>4.56 ± 0.51</td>
<td>2.01 ± 0.24</td>
<td>1.44 ± 0.079</td>
<td>2.011 ± 0.333</td>
</tr>
<tr>
<td>0.264</td>
<td>34.78 ± 0.87</td>
<td>29.53 ± 1.63</td>
<td>4.31 ± 0.47</td>
<td>1.94 ± 0.24</td>
<td>1.72 ± 0.093</td>
<td>2.333 ± 0.381</td>
</tr>
<tr>
<td>0.362</td>
<td>20.92 ± 0.29</td>
<td>17.79 ± 1.11</td>
<td>3.47 ± 0.37</td>
<td>2.59 ± 0.44</td>
<td>2.21 ± 0.107</td>
<td>1.775 ± 0.238</td>
</tr>
<tr>
<td>0.446</td>
<td>19.06 ± 0.29</td>
<td>12.31 ± 0.59</td>
<td>1.81 ± 0.17</td>
<td>1.96 ± 0.21</td>
<td>2.53 ± 0.056</td>
<td>2.664 ± 0.156</td>
</tr>
<tr>
<td>0.579</td>
<td>16.62 ± 0.31</td>
<td>13.7 ± 0.56</td>
<td>2.19 ± 0.21</td>
<td>2.13 ± 0.23</td>
<td>3.15 ± 0.101</td>
<td>2.070 ± 0.176</td>
</tr>
<tr>
<td>0.634</td>
<td>14.10 ± 0.41</td>
<td>12.4 ± 0.90</td>
<td>1.89 ± 0.18</td>
<td>2.03 ± 0.24</td>
<td>2.88 ± 0.186</td>
<td>2.107 ± 0.349</td>
</tr>
<tr>
<td>0.681</td>
<td>7.85 ± 0.64</td>
<td>11.14 ± 1.35</td>
<td>1.80 ± 0.17</td>
<td>2.15 ± 0.33</td>
<td>1.71 ± 0.111</td>
<td>1.354 ± 0.136</td>
</tr>
</tbody>
</table>

$^a$Time taken for maximum nucleation rate to be achieved. $^b$Time window for nucleation. $^c$Total number of critical aggregates. $^d$Maximum nucleation rate. $^e$Growth rate. $^f$Avrami exponent.
A combined nucleation function for all the trials is plotted in Figure 1-17. Figure 1-17 and Table 1-3 reveal that as the TOABr concentration was increased the width of the time window for nucleation $\Delta t_n$ first decreased from $30 \pm 1$ min, and then remained at about $12 \pm 1$ min upon reaching a minimum for $[\text{TOABr}] \geq 0.446$ M. As the TOABr concentration was increased, the nucleation function also progressively shifted to shorter times. This shift is quantified by $\tau_n$, the time at which $\Gamma_{\text{max}}$ was achieved. Table 1-3 shows that $\tau_n$ varied from $38 \pm 1$ min at low $[\text{TOABr}]$ to $8 \pm 1$ min at high $[\text{TOABr}]$. Therefore, increasing TOABr concentration increased the rates of and decreased the time period for aggregative nucleation.

![Figure 1-17. Nucleation functions for the kinetic trials conducted at various TOABr concentrations. The individual [TOABr] values are given in the inset legend.](image)

Interestingly, in most of the trials the maximum aggregative-nucleation rate $\Gamma_{\text{max}}$ remained fairly constant near $(2.0 \pm 0.2) \times 10^{13}$ s$^{-1}$. Only the trial at $[\text{TOABr}] = 0.362$ M deviated slightly from this pattern, having a $\Gamma_{\text{max}} = (2.6 \pm 0.4) \times 10^{13}$ s$^{-1}$. However, even this
apparent difference was small, and within the error of the measurement (see Figure 1-18). Even so, the pattern observed here (Figure 1-17) differed considerably from that reported by Wette\textsuperscript{27} (Figure 1-3), for which the shift of the nucleation function to shorter time and narrower widths was accompanied by a significant, progressive increase in $\Gamma_{\text{max}}$.

![Figure 1-18](image)

**Figure 1-18.** Plots of the maximum nucleation rate $\Gamma_{\text{max}}$ (black squares, left axis) and growth rate $k_g$ (red circles, right axis) vs. TOABr concentration.

**Fitting the nanocrystal growth kinetics.** The size-vs.-time plots for nanocrystal growth typically exhibit sigmoidal profiles like that in Figure I-4.\textsuperscript{38-42,43,44-46} The initial induction-like period is associated with nucleation, which is the formation of critical aggregates in the case of aggregative growth. The nucleation regime is followed by an active growth regime in which supercritical nanocrystals, derived from the critical aggregates, grow by aggregation with primary nanocrystals, until the primary nanocrystals are consumed. Ostwald ripening may occur at the conclusion of active growth under appropriate conditions.
We did not observe Ostwald ripening in our experiments until later times, beyond the end of our kinetic trials.

The growth profiles as presented in plots of nanocrystal mean volume $\bar{V}$ vs. time were sigmoidal. The $\bar{V}(t)$ data were extracted from the nanocrystal-volume distributions determined at time intervals, as described above, and scaled by the final mean nanocrystal size $\bar{V}_\text{lim}$. Thus, nanocrystal growth was followed by plotting $\bar{V}(t)/\bar{V}_\text{lim}$ vs. $t$. The growth kinetics so obtained were fit to a KJMA equation $^{47-50}$ (eq 3) having two fitting parameters, a growth-rate parameter $k_g$ and an Avrami exponent $n$. The parameter $\bar{V}_1$ is the primary nanocrystal mean volume. Kinetic data collected at a TOABr concentration of 0.145 M and the resulting fitted curve are plotted in Figure 1-19. Kinetic fits were similarly obtained for the trials conducted for the range of TOABr concentrations used. The results are plotted in Figures 1-20 to 1-25.

$$\frac{\bar{V}(t)}{\bar{V}_\text{lim}} = \frac{\bar{V}_1}{\bar{V}_\text{lim}} + \left(1 - \frac{\bar{V}_1}{\bar{V}_\text{lim}}\right) \left(1 - \exp\left(-k_g t\right)^n\right)$$  \hspace{1cm} (3)
Figure 1-19. Kinetic data and the eq-3 fit for the trial conducted at [TOABr] = 0.145 M. $\bar{V}(t)$ is the nanocrystal mean volume at a specific time, and $\bar{V}_{\text{lim}}$ is the final nanocrystal mean volume.

Figure 1-20. Kinetic data and the eq-3 fit for the trial conducted at [TOABr] = 0.264 M. $\bar{V}(t)$ is the nanocrystal mean volume at a specific time, and $\bar{V}_{\text{lim}}$ is the final nanocrystal mean volume.
Figure 1-21. Kinetic data and the eq-3 fit for the trial conducted at [TOABr] = 0.362 M. \( V(t) \) is the nanocrystal mean volume at a specific time, and \( V_{lim} \) is the final nanocrystal mean volume.

Figure 1-22. Kinetic data and the eq-3 fit for the trial conducted at [TOABr] = 0.446 M. \( V(t) \) is the nanocrystal mean volume at a specific time, and \( V_{lim} \) is the final nanocrystal mean volume.
Figure 1-23. Kinetic data and the eq-3 fit for the trial conducted at [TOABr] = 0.579 M. $\bar{V}(t)$ is the nanocrystal mean volume at a specific time, and $\bar{V}_{\text{lim}}$ is the final nanocrystal mean volume.

Figure 1-24. Kinetic data and the eq-3 fit for the trial conducted at [TOABr] = 0.634 M. $\bar{V}(t)$ is the nanocrystal mean volume at a specific time, and $\bar{V}_{\text{lim}}$ is the final nanocrystal mean volume.
Figure 1-25. Kinetic data and the eq-3 fit for the trial conducted at [TOABr] = 0.264 M. \( \bar{V}(t) \) is the nanocrystal mean volume at a specific time, and \( \bar{V}_{\text{lim}} \) is the final nanocrystal mean volume.

All sets of kinetic data collected as a function of TOABr concentration are plotted in Figure 1-26, with their eq-3 fits. The fitted \( k_g \) and \( n \) values are recorded in Table 1-3, and the \( k_g \) values are also plotted in Figure 1-18. Although the quality of the fits was sensitive to the value of the Avrami exponent \( n \), the fitted values of \( k_g \) were insensitive to this parameter over \( n = 1-3 \) as tabled in Table 1-4, the typical range for the Avrami exponent.\(^{51}\) Thus, we considered the \( k_g \) values to be a robust indicator of the relative growth rates.
Figure 1-26. Kinetic data and the eq-3 fits for trials conducted at various TOABr concentrations. The individual [TOABr] values are given in the inset legends. (a) 0.145-0.579 M; (b) 0.579-0.681 M.
Table 1-4. Relative insensitivity of $k_g$ to the Avrami exponent $n$. The $n$ values are between 1.5 and 3, for the kinetic data obtained from the thermal coarsening conducted at various [TOABr].

<table>
<thead>
<tr>
<th>$n$</th>
<th>[0.145 M]</th>
<th>[0.264 M]</th>
<th>[0.362 M]</th>
<th>[0.446 M]</th>
<th>[0.579 M]</th>
<th>[0.634 M]</th>
<th>[0.681 M]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_g$ (x 10^{-2} s^{-1})</td>
<td>$k_g$ (x 10^{-2} s^{-1})</td>
<td>$k_g$ (x 10^{-2} s^{-1})</td>
<td>$k_g$ (x 10^{-2} s^{-1})</td>
<td>$k_g$ (x 10^{-2} s^{-1})</td>
<td>$k_g$ (x 10^{-2} s^{-1})</td>
<td>$k_g$ (x 10^{-2} s^{-1})</td>
</tr>
<tr>
<td>1.5</td>
<td>1.48 ± 0.09</td>
<td>1.28 ± 0.06</td>
<td>2.23 ± 0.12</td>
<td>2.10 ± 0.05</td>
<td>2.95 ± 0.10</td>
<td>2.91 ± 0.21</td>
<td>1.75 ± 0.10</td>
</tr>
<tr>
<td>2</td>
<td>1.44 ± 0.08</td>
<td>1.61 ± 0.06</td>
<td>2.20 ± 0.10</td>
<td>2.34 ± 0.05</td>
<td>3.13 ± 0.09</td>
<td>2.88 ± 0.19</td>
<td>1.88 ± 0.09</td>
</tr>
<tr>
<td>2.5</td>
<td>1.42 ± 0.07</td>
<td>1.78 ± 0.06</td>
<td>2.17 ± 0.08</td>
<td>2.49 ± 0.04</td>
<td>3.25 ± 0.08</td>
<td>2.88 ± 0.17</td>
<td>1.99 ± 0.09</td>
</tr>
<tr>
<td>3</td>
<td>1.41 ± 0.06</td>
<td>1.88 ± 0.06</td>
<td>2.15 ± 0.07</td>
<td>2.59 ± 0.04</td>
<td>3.32 ± 0.07</td>
<td>2.90 ± 0.16</td>
<td>2.06 ± 0.08</td>
</tr>
</tbody>
</table>

In principle, the $k$ parameters extracted from KJMA analyses convolve nucleation and growth rates.\textsuperscript{50,52} However, we will show in subsequent discussions that $k_g$ here is strongly associated with growth rates, and imperceptibly or only weakly to nucleation rates. The results reveal that the growth rates first increased, passed through a maximum, and then decreased with increasing [TOABr]. The minimum and maximum $k_g$ values differed by only an approximate factor of 2 (Table 1-3).

Evidence for aggregative nucleation and growth. We have argued here for a nonclassical process in which nucleation proceeds by formation of a critical aggregate of primary nanocrystals. Growth then proceeds by the subsequent addition of primary nanocrystals to the critical and supercritical aggregates. One must also consider if growth proceeds instead by an Ostwald-ripening mechanism in which primary particles dissolve and are re-precipitated onto larger nanocrystals, presumably the larger of the primary nanocrystals in the initial CSD.

Therefore, we used TEM and high-resolution TEM (HRTEM) to distinguish between an aggregative-growth and Ostwald-ripening processes. In the former case, nucleation and growth should \textit{initially} produce primary-nanocrystal aggregates, and then polycrystalline
nanoparticles, with their constituent domains derived from the primary nanocrystals. In the latter case, the growing nanoparticles should be single nanocrystals, because they would have grown from deposition of molecular nutrients onto single-crystal primary nanoparticles.

We did find small aggregates of primary nanocrystals in the early time TEM images of coarsening trials (Figure 1-27). However, these aggregates may have formed on the TEM grid rather than under coarsening conditions. A dominant characteristic of the early time images was the coexistence of small numbers of distinctly larger nanoparticles with the abundant primary nanocrystals (Figure 1-28), suggesting that nanocrystal coalescence followed rapidly after primary-nanocrystal aggregate formation. Consequently, we determined the internal texture of the larger, supercritical nanoparticles as described below.

Figure 1-27. TEM images of aliquots removed at early times from coarsening experiments (<<τ_n). The red arrows identify small aggregates of primary nanocrystals (see text).
Figure 1-28. TEM images of aliquots removed at early times from coarsening experiments ($<\tau_n$), but not as early as those imaged in Figure 1-27. A dominant characteristic of such images was the coexistence of small numbers of distinctly larger nanoparticles with the abundant primary nanocrystals.

Figure 1-29 contains HRTEM images of Au nanoparticles after approximately 10 min under coarsening conditions. The images reveal polycrystalline domain structures, wherein the number and mean size of the domains are consistent with the mean primary nanocrystal. For example, the nanoparticle in Figure 1-29a has a diameter of 4 nm, and a mean domain size of 1.5 nm, which compares favorably to the mean primary nanocrystal size of 1.7 nm. An aggregated nanoparticle having a diameter of 4 nm should consist of 13 primary-nanocrystal-derived domains, 8 of which are discernible in Figure 1-29a. The remainder is likely obscured by overlap, especially near the center of the nanoparticle image where the depth trajectory is the longest.
Figure 1-29. High-resolution TEM images of polycrystalline Au nanoparticles obtained after coarsening for ca. 10 min. The line drawings depict the crystalline domains that can be discerned in the images.

Only a fraction of the early time nanoparticles exhibited polycrystalline structures; the rest were single crystals. Although we did not examine a statistically significant number of nanoparticles in the HRTEM study, we estimate that 20-40% were polycrystalline. We surmised that the remaining nanoparticles had already undergone coalescence to single
crystals within the 10 min growth period. Thus, we propose that all of the nanoparticles were initially polycrystalline.

HRTEM images of the nanoparticles after 60 min of coarsening established that at least 95% were single crystals. A small fraction (≤ 5%) exhibited multiply twinned structures (see Figure 1-30). The multiply twinned structures likely evolved from the initial polycrystalline architectures as suggested by Turkevich and Uyeda, because they are unlikely to have developed later within initially single-crystal nanoparticles. The results suggested that over time most or all of the initially polycrystalline nanoparticles coalesced to single crystals. The HRTEM results are therefore most consistent with aggregative growth. If growth was by Ostwald ripening, none of the early time nanoparticles should have possessed polycrystalline structures.

**Figure 1-30.** High-resolution TEM image of a multiply twinned Au nanoparticle obtained after coarsening for ca. 80 min.
Further evidence of aggregative nucleation and growth was the observation of bimodal CSDs at intermediate stages of coarsening. Figure 1-31 is a representative TEM image taken from a kinetics run a few minutes after $\tau_n$, the time at which $\Gamma_{\max}$ was achieved. The image clearly shows a population of small, primary nanocrystals, and a second population of much larger nanoparticles, with few nanoparticles of intermediate size. The CSD corresponding to Figure 1-31 is shown in Figure 1-32. Aggregative processes are known to produce such bimodal distributions,\textsuperscript{35,58,59-67} because aggregation introduces a second population of particles that are distinctly larger than the primary particles.\textsuperscript{68,61}

\textbf{Figure 1-31.} A TEM image from a coarsening trial at an intermediate time showing a bimodal distribution of coarsened and primary nanocrystals. Note that the coarsened (center) and primary (left and right) nanocrystals are largely segregated into separate regions of the TEM grid. The primary-nanocrystal regions are identified by arrows. The scale bar is 50 nm.
Figure 1-32. Size distribution histogram of Au nanoparticles taken a few minutes after maximum nucleation rate ($\tau_n$) was achieved. The CSD is strongly bimodal, with the smaller-size mode corresponding to primary nanocrystals, and the larger-size mode to the nanoparticles growing by aggregative processes.

In contrast, Ostwald ripening generally proceeds by a unimodal, self-similar CSD that broadens and shifts with time, but does not bifurcate.\textsuperscript{44,67-72} The generation of a bimodal distribution by Ostwald ripening requires special circumstances, specifically, a mass-exchange-rate discontinuity at a critical nanocrystal size.\textsuperscript{73} As described in the Discussion, one origin of such a rate discontinuity is a nanocrystal-morphology change occurring at a specific size. Such a special circumstance does not exist here. The bimodality we observed resulted from the emergence and evolution of the peak at the critical-aggregate size $V_{\text{crit}}$ in the CSDs (see Figures 1-3 to 1-9), which coexisted with the primary nanocrystals until they were all consumed by aggregative growth.

Finally, the sigmoidal growth kinetics we observed (Figures 1-19 to 1-25) are inconsistent with the LSW model for equilibrium Ostwald ripening, which asserts a linear
growth in nanoparticle volume $\mathcal{F}$ vs. time.$^{53,54}$ As noted above, we did observe Ostwald ripening to occur after very long times, considerably beyond the conclusion of our kinetic trials (Figure 1-33). Additionally, we observed Ostwald ripening to occur in TEM specimens that had been allowed to stand for several hours before analysis. However, the combined results of nanoparticle structure, the evolution of the CSDs, and the growth kinetics argue strongly against Ostwald ripening as the dominant growth mechanism during the active-growth period.

![Figure 1-33](image)

**Figure 1-33.** A TEM image of an aliquot removed at a very late time from a coarsening experiment ($\gg\gg\tau_0$), roughly 14 h beyond the conclusion of the active growth period. Extensive Ostwald ripening is evident in the image.

**Use of a KJMA expression to assess growth rates.** KJMA or Avrami models, such as eq 3, are rigorously applicable to the kinetics of certain solid-state phase transformations.$^{50-52}$ However, KJMA analyses have also been applied to solution-based or melt crystallization of zeolites,$^{76}$ lipids,$^{77-79}$ polymers,$^{80,81}$ β-haematin,$^{82}$ and colloidal crystals,$^{27}$ and to nanocrystal
growth. As in eq 3, KJMA expressions generally contain two kinetic parameters: an Avrami exponent \( n \), the value of which is often related to the nucleation mechanism and dimensionality of growth, and a rate parameter \( k \) that convolves nucleation and growth rates. Although the rates of nucleation and growth are not separately parameterized, we show below that our \( k_g \) (eq 3) is most strongly dependent on growth behavior, and is thus a reliable indicator of relative growth rates.

Figure 1-34 plots a set of kinetic data ([TOABr] = 0.264 M) and the eq-3 fit using the optimized values for \( k_g \) and \( n \). Two additional curves are plotted, one in which \( k_g \) has been increased by 10% from the optimal value, and one in which \( k_g \) has been decreased by 10% (both at the original optimized \( n \)). The reader will note that the fits to the initial induction period, associated with nucleation, are scarcely affected by the variations in the \( k_g \) value. However, the fits in the rising portion of the sigmoidal data, the active growth regime, are strongly affected. The \( k_g \) values at ±10% of the optimal value provide considerably poorer fits to the growth-regime data. We therefore conclude that \( k_g \) is much more strongly reflective of growth rates than of nucleation rates.
Figure 1-34. Kinetic data (red squares) from Figure 1-20, and the eq-3 fit (red curve) using the optimized values of $k_g$ and $n$. Equation-3 fits are also provided in which $k_g$ has been increased (black curve) and decreased (green curve) by 10% from the optimized value (while $n$ is held at its optimized value). These curves show that $k_g$ functions primarily as a fitting parameter for the rapidly rising, active-growth regime in the kinetic data.

Although attractive in its simplicity, the KJMA analysis used here (eq 3) is incomplete, as it follows only the growth of the mean nanoparticle size and not the evolution of the entire CSD. As shown here (Figure 1-1) and elsewhere, CSDs evolve in time according to mechanistically informative patterns, and complete kinetic studies of nanocrystal growth should explicitly address them. Distributed-kinetics approaches follow the kinetic fate of every size in a time-evolving CSD by assuming a mechanism, encoding the size dependences of the kinetic parameters into population-balance equations, and simulating or fitting the CSDs as a function of time. However, such approaches are computationally intensive and so are neither convenient nor generally accessible to the nanocrystal-synthesis community.

We use the simple analytical expression in eq 3 only to obtain relative quantitative comparisons of growth rates as a function of TOABr concentration. We note that the same
information can be assessed qualitatively merely by visual inspection of the slopes of the rising portions of the kinetic plots in Figure 1-26. Other analytical models also exist for fitting nanoparticle-growth data,\textsuperscript{45,46} one of which will be investigated in a subsequent paper.\textsuperscript{86} Furthermore, not all nanocrystal-growth data can be fit by a KJMA expression or other analytical models.\textsuperscript{88} Therefore, the relative growth rates extracted with eq 3 are used below in only a careful, limited manner.

**Exclusion of Ostwald ripening as the origin of the observed bimodal CSDs.** As noted above, theoretical studies indicate that Ostwald ripening is generally incapable of producing a bimodal size distribution,\textsuperscript{67,72} unless a discontinuity exists in interparticle-exchange rates.\textsuperscript{73} Studies of particle-coarsening on surfaces have found that such rate discontinuities can be generated by particle-shape changes, such as between domed and faceted morphologies, occurring at a critical size.\textsuperscript{89-92} Bimodal size distributions result, as one morphology ripens faster than the other. Similar observations have been made for nanocrystals ripened under hydrothermal conditions.\textsuperscript{93} A rate discontinuity induced by substrate-particle strain has also been proposed as the origin of bimodal CSDs developed by Ostwald ripening.\textsuperscript{94} However, there is no substrate-particle strain or distinct morphology changes in our Au-nanocrystal ripening experiments, ruling out Ostwald ripening as the origin of the early time bimodal CSDs.

Theoretical\textsuperscript{95} and experimental \textsuperscript{96,97} studies also show that bimodal distributions initially formed by various means can be *accentuated* by Ostwald ripening. That is, the smaller mode shrinks in particle size and number as the larger mode increases in particle size and number. The initial bimodal CSDs can be generated by successive nutrient dosing,\textsuperscript{97} by successive heat treatments at different temperatures,\textsuperscript{98} by secondary nucleation processes,\textsuperscript{99}
or simply by combining two unimodal populations. In such cases, Ostwald ripening is not the origin of the bimodal distributions, but does increase the separation between the two modes.

Despite the theoretical findings against it, experimental observations of bimodal size distributions generated in coarsening studies on surfaces are occasionally attributed to Ostwald ripening, or proposed as evidence of it. Indeed, it is tempting to imagine that smaller particles shrinking and larger particles growing could generate a bifurcation and thus bimodality in an initially unimodal CSD. However such claims are not supported theoretically. Except under the special circumstances noted above, the shrinking and growing particles remain within a single, evolving, self-similar, unimodal CSD.

We contend that the observations of bimodal distributions attributed to Ostwald ripening result instead from the alternative origins described above. In one case, strain appears to have generated a rate discontinuity. In other cases, bimodal distributions are initially present. In other cases, Ostwald ripening has been assumed, evidence for aggregation and coalescence has been ignored, or aggregation and coalescence has not been compellingly excluded. Therefore the generation of a bimodal CSD may be properly attributed to aggregative growth, but not to Ostwald ripening.

**Kinetic evidence for the electrostatic stabilization of thiolate-capped Au nanocrystals.** Thiolate-capped Au nanocrystals are sterically stabilized; that is, solvent dispersions of nanocrystals are stable against flocculation because of steric interactions between the ligand monolayer coatings on adjacent nanocrystals. However, Schiffrin and coworkers demonstrated that Au nanocrystals prepared by the two-phase Brust synthesis, employed here for the primary nanocrystals, retain significant amounts of TOABr, a
synthetic phase-transfer agent.\textsuperscript{105} They proposed an electric double-layer-like structure (Fig. 3 in Ref. 105) with bromide ions bound to the nanocrystal surface interspersed with the thiolates, and with a second, outer shell of $n$-octyl$_4$N\textsuperscript{+} counter ions (Scheme 1-1, left side). Schiffrin and coworkers used this structure to rationalize the low solubility of the Au-nanocrystal material retaining TOABr relative to that from which the TOABr had been exhaustively removed. They argued that the electric double-layer-like structure resulting from TOABr retention produced electrostatic interactions that increased the lattice energy (stabilization) of the solid, and thereby decreased its solubility (dispersibility).\textsuperscript{105}
Scheme 1-1. Schematic depiction of the collapse of the electric double layer about the Au nanocrystals with a sufficient amount of added TOABr.

The yellow region surrounding the gold nanocrystal core represents the thiolate monolayer, and the light-blue region represents the double-layer (the extent of the octyl\(_4\)N\(^+\)counterion atmosphere). The octyl\(_4\)N\(^+\) ions are depicted by plus signs, and the Br\(^-\) ions attached to the Au surfaces by minus signs. At low ionic strength (left) the octyl\(_4\)N\(^+\)counterion atmosphere is extended due to mutual octyl\(_4\)N\(^+\) ion repulsions. The extended octyl\(_4\)N\(^+\)counterion atmospheres on adjacent nanoparticles repel one another, preventing the close approach of nanoparticles, and thus inhibiting their aggregation. At high ionic strength (right) the double layer collapses due to screening, and the counterion atmosphere about each nanoparticle shrinks dramatically, allowing the close approach of nanoparticles. Only the steric barrier due to the thiolate monolayers remains to provide (a lesser) stabilization against aggregation.
We are now extending this electrostatic-stabilization model\textsuperscript{105} to account for the behavior of the thiolate-capped Au nanocrystals in solvent dispersion. These nanocrystals exhibited excellent dispersibility in the solvent system we employed. Standard DLVO theory asserts that such nanocrystals would also be electrostatically stabilized in dispersion, against aggregation and coalescence, by interparticle repulsions between the octyl\textsubscript{4}N\textsuperscript{+} outer shells (counter-ion “atmospheres” on adjacent nanocrystals, Scheme 1).\textsuperscript{106} However, the degree of such electrostatic stabilization is dependent on the ionic strength of the medium (Scheme 1). We present kinetic evidence from the nucleation functions (Figure 1-17) in support of this proposal.

As noted in the Results, increasing TOABr concentrations caused the nucleation functions to progressively narrow and shift to earlier times (as quantified by $\Delta t_n$ and $\tau_n$, respectively, in Table 1-3). The results showed that added TOABr accelerated the aggregative-nucleation process. The narrowing of the nucleation function was dramatic at the lower TOABr concentrations, and then achieved a near-constant minimum of $\Delta t_n \approx 12$ min at higher TOABr concentrations. We interpret this behavior to indicate a collapse of the electric double layer at a sufficient TOABr concentration, removing the electrostatic barrier for aggregative nucleation.

DLVO theory establishes that the Debye length, the thickness of the counter-ion atmosphere (electric double layer), depends on the ionic strength of the medium (Scheme 1).\textsuperscript{106} At low ionic strength the counter-ion atmosphere is diffuse due to mutual electrostatic repulsions between the counter ions (here, octyl\textsubscript{4}N\textsuperscript{+} ions), preventing close approach of adjacent particles. At higher ionic strength the counter-ion atmosphere shrinks and eventually collapses because the mutual repulsions are screened, and the electrostatic barrier
to particle aggregation is thus removed\textsuperscript{29,31,107}. At this point, the remaining barrier to aggregation (and thus nucleation) is the steric barrier presented by the intact thiolate monolayer on each nanoparticle.

We propose that the TOABr-derived electric double layer about the primary Au nanocrystals collapses completely at [TOABr] = 0.446 M (Table 1-1, Figure 1-17), resulting in the minimization of $\Delta t_n$. The narrowing of the nucleation function is rationalized by prior studies of reaction-limited vs. diffusion-limited aggregation (RLCA and DLCA, respectively)\textsuperscript{69,108}. The “pure” RLCA and DLCA mechanisms form the limits of a spectrum of intermediate mechanisms, with the broadest final particle-size distribution generally obtained at the RLCA limit, and the narrowest at the DLCA limit\textsuperscript{69,108}. The narrowest final particle-size distribution argues for the narrowest nucleation function. In the present case, a steric barrier due to the thiolate monolayer remains, and so the DLCA limit is approached at higher TOABr concentrations, but is presumably not achieved.

Because the electrostatic barrier disappears at [TOABr] = 0.446 M, further narrowing of the nucleation function is not achieved at even higher TOABr concentrations. We speculate that the continued decrease in $\tau_n$ is a secondary ionic-strength effect on the remaining steric barrier. The observed dependence of the nucleation kinetics on TOABr concentration constitutes strong evidence of the (partial) electrostatic stabilization of thiolate-capped Au nanocrystals\textsuperscript{105}.

**Nucleation control of the final nanocrystal size and size distribution.** As noted above, the narrowest nucleation function, parameterized by $\Delta t_n$, should correlate with the narrowest final CSD (that obtained at the end of the active-growth period). Figure 1-35 plots the relative standard deviation in the final CSD vs. [TOABr], which shows a minimum near
[TOABr] = 0.446 M, the lowest concentration at which the nucleation function obtained a near-constant minimum $\Delta t_n$. The minimum relative standard deviation of 0.057 (or 5.7% of the final mean nanocrystal size) is very close to the minimum value predicted theoretically for the liquid-phase synthesis of nanoparticles (7.1%). At TOABr concentrations above 0.579 M, the final CSDs broaden, although the nucleation functions do not (Figure 1-35). We attribute this broadening to the significant solvent viscosity increases at high TOABr concentrations. The results strongly suggest that nucleation control of the width of the final size distribution was achieved.

**Figure 1-35.** Plots of the relative standard deviation in the final nanocrystal diameter distribution (black circles, left axis) and the time window for nucleation $\Delta t_n$ (red squares, right axis) vs. TOABr concentration. The relative standard deviation is the standard deviation in the diameter divided by the final mean nanocrystal diameter.

We argued above that the final nanocrystal mean size should be determined by the total amount of Au present and $N$, the number of critical aggregates formed, which is the area under the nucleation function. Equation 2 on page 29, establishes that the width ($\Delta t_n$) and
height ($\Gamma_{\text{max}}$) of the nucleation function are equally influential in determining $N$. However, in the present work the minimum and maximum values of $\Delta t_n$ varied by a factor of 3, whereas the minimum and maximum values of $\Gamma_{\text{max}}$ varied by only a factor of 1.29 and were within experimental error of one another (Figure 1-18). Consequently, we would expect the final nanocrystal mean size to also correlate most strongly here with $\Delta t_n$, as does the width of the final CSD (see above).

The near-constant $\Gamma_{\text{max}}$ values contrast with those reported by Wette and coworkers\textsuperscript{27} (Figure I-5), in which the narrowing and shifting of the nucleation function to earlier times were accompanied by progressive increases in $\Gamma_{\text{max}}$. Although the time-dependent nucleation rates generally increased here with TOABr concentration, as indicated by the progressively decreasing $\tau_n$ values, $\Gamma_{\text{max}}$ did not systematically increase (Figures 1-17, 1-18 and Table 1-3), as in Figure I-5. However, Wette and coworkers achieved increases in $\Gamma_{\text{max}}$ by increasing the initial primary-particle volume fraction, which was only incidentally varied over a small range in our study. We also note that two opposing influences operate on $\Gamma_{\text{max}}$: the rate at which the critical aggregates are formed, and the rate at which they are consumed by growth ($k_g$). Figure 1-18 shows that $k_g$ increased steadily with increasing TOABr concentration, until the highest concentrations, at which the viscosity increased dramatically. We surmise that the increasing growth rates constrained $\Gamma_{\text{max}}$ to the observed near-constant values. As a result $N$, and thus the final nanocrystal mean size, should correlate with $\Delta t_n$. As $\Delta t_n$ decreases $N$ also decreases, and the final nanocrystal mean size should increase, as a constant amount of Au is divided among fewer nanocrystals. This expectation is confirmed in Figure 1-36a, which plots the final nanocrystal mean size and $\Delta t_n$ vs. [TOABr]. Remarkably, the two
curves are nearly mirror images of one another, indicating a strong correlation of final size and $\Delta t_n$.

**Figure 1-36.** (a) Plots of the final nanocrystal mean diameter (black squares, left axis) and $\Delta t_n$ (red circles, right axis) vs. TOABr concentration. (b) Plot of the final nanocrystal mean diameter vs. $\Delta t_n$. The curve is the theoretical dependence of the mean $d_{\text{final}}$ on $\Delta t_n$ assuming a constant, averaged value for $\Gamma_{\text{max}}$ (see text).
This strong correlation is further evidenced in Figure 1-36b, which plots the final nanocrystal mean size vs. $\Delta t_n$. The curve in Figure 1-36b is the theoretical dependence of the final mean diameter on $\Delta t_n$ assuming a constant value for $\Gamma_{\text{max}}$. The derivation of this function is shown in Scheme 1-2 below. The assumed value is the average of the $\Gamma_{\text{max}}$ values in Table 1-3. The agreement between the data and curve establish convincingly that the final nanocrystal mean size is controlled primarily by the width of the nucleation function. The combined results confirm that both the width of the final CSD and the final mean size were under nucleation control.

**Scheme 1-2. Derivation of the function plotted in Figure 1-36b for theoretical dependence of the final mean nanocrystal diameter on $\Delta t_n$:**

A mean $\Gamma_{\text{max}}$, determined from the values in Table 1, is assumed:

$$\Gamma_{\text{max}} = 2.1157 \times 10^{13} \text{ s}^{-1}$$

The number $N$ of nanocrystals is calculated by eq 2:

$$N = 1.2533(\Gamma_{\text{max}} \text{ s}^{-1})(\Delta t_n \text{ min})(60 \text{ s/min}) = 75.198(\Gamma_{\text{max}})(\Delta t_n)$$

The total volume of Au ($V_{\text{tot}}$) used in each trial is calculated by assuming the bulk density:

$$V_{\text{tot}} = 2.808 \times 10^{18} \text{ nm}^3$$

The final mean nanocrystal volume is calculated:

$$\bar{V}_{\text{fin}} = \frac{V_{\text{tot}}}{N}$$

The final mean nanocrystal volume is related to the final mean nanocrystal diameter:

$$\bar{V}_{\text{fin}} = \frac{4}{3} \pi \bar{d}_{\text{fin}}^3 = \frac{4}{3} \pi \left( \frac{\bar{d}_{\text{fin}}}{2} \right)^3 = \frac{\pi}{6} \bar{d}_{\text{fin}}^3$$

Substituting:

$$\frac{V_{\text{tot}}}{N} = \frac{V_{\text{tot}}}{75.198(\Gamma_{\text{max}})(\Delta t_n)} = \frac{\pi}{6} \bar{d}_{\text{fin}}^3$$

Solve for the final mean nanocrystal diameter:
\[ d_{\text{fin}} = \left[ \frac{6V_{\text{tot}}}{75.198\pi(\Gamma_{\text{max}})(\Delta t_n)} \right]^{1/3} \]

Insert assumed values (see above) and simplify:

\[ d_{\text{fin}} \text{ (nm)} = \left[ \frac{3371.2}{\Delta t_n \text{ (min)}} \right]^{1/3} \]

Unfortunately, the final nanocrystal size was varied over only a small range in this study, 4.9-6.7 nm, which is not synthetically useful. To gain synthetic utility, \( N \) would be purposefully varied over a much larger range. Ideally, one would maintain a minimized \( \Delta t_n \) by using an optimal amount of salt or other nucleation-control additive, to ensure an optimally narrow final CSD. Therefore, \( N \) would ideally be controlled by variations of \( \Gamma_{\text{max}} \), which thus becomes the preferred size-control parameter.

As revealed by the results above, we have not yet determined how to purposefully vary \( \Gamma_{\text{max}} \). However, \( \Gamma_{\text{max}} \) has been shown to increase systematically with increasing primary-particle volume fraction\(^{27} \) (Figure I-5) or nutrient concentration.\(^{56} \) In an analogous field, the rate of formation of gas-phase clusters is a power-law function of pressure, \( P^\alpha \) with \( 1 < \alpha < 3 \).\(^{110-112} \) Thus, the nucleation of gas-phase clusters increases rapidly with pressure. We expect to find a similar relationship between \( \Gamma_{\text{max}} \) and primary-particle volume fraction or nutrient concentration, providing directions for further research.

**Conclusions**

As noted above, we were initially motivated to pursue these studies by the reports of Zhong and coworkers that small, thiolate-capped Au nanocrystals having broad initial CSDs...
could be ripened, in the presence of the coarsening agent TOABr, to larger nanocrystals having narrow CSDs.\textsuperscript{23,24} We were surprised by these results because they seemed inconsistent with standard Ostwald ripening, the mechanism we assumed to be operative. However, Zhong and coworkers suggested an aggregative-growth mechanism, which we now confirm by the results herein.

The primary evidence against Ostwald ripening was the observation of bimodal size distributions at early times, polycrystalline particles, and sigmoidal growth kinetics, as detailed above. However, Ostwald ripening is not a nucleation-driven process. If nanoparticle growth occurred by Ostwald ripening here, then there would have been no critical size and no nucleation function. In that event we could not have observed the strong correlation between the final nanoparticle mean size and size distribution with $\Delta t_n$, which is shown in Figures 1-35 and 1-36.

Schiffrin and coworkers first reported that thiolate-capped Au nanocrystals persistently retain TOABr, and proposed an electric-double-layer-like structure.\textsuperscript{105} Here we found that the aggregative growth of thiolate-capped Au nanocrystals is largely governed by the electric-double-layer stabilization of the nanocrystals. Addition of TOABr collapses the electric double layer, increasing the rates of aggregative nucleation and sharpening the aggregative-nucleation function. Because the maximum nucleation rate $\Gamma_{\text{max}}$ is insensitive to the TOABr concentration, the width of the nucleation function $\Delta t_n$ controls both the final size and size distribution of the ripened nanocrystals.

This work demonstrates that gaining control over the nucleation function ($\Gamma_{\text{max}}$ and $\Delta t_n$) is the key to achieving rational synthetic control of nanocrystal mean sizes and the minimization of size distributions. In this study we achieved systematic control over the
width of the nucleation function ($\Delta t_n$), but not its height ($\Gamma_{\text{max}}$). Ideally, nanocrystal size distributions will be minimized by minimizing $\Delta t_n$, and nanocrystal sizes will be manipulated by purposeful variations in $\Gamma_{\text{max}}$. Thus, important synthetic advances in nanocrystal synthesis will be possible when $\Gamma_{\text{max}}$ can be systematically controlled.

Finally, the results suggest the great synthetic potential of aggregative growth. One may potentially vary aggregative-nucleation rates, and therefore the nucleation function, by varying any factor that influences nanocrystal stability, including the use of salts and other additives, the presence of stabilizing agents such as ligands and polymers, and variations in precursor or primary-particle concentrations, solvents, and temperature. Nucleation rates in classical nucleation and growth are not as predictably manipulated, and the corresponding nucleation functions cannot presently be experimentally determined. Thus, aggregative growth should allow means of synthetic control that are not otherwise available.

**Experimental Section**

**General methods and materials.** Decanethiol, tetraoctylammonium bromide (TOABr), hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$·3H$_2$O), sodium borohydride (NaBH$_4$), toluene, ethanol (EtOH), and diphenylmethane were purchased from Aldrich and used as received. All preparations and coarsening (growth) experiments were conducted under an ambient atmosphere. The coarsening experiments were conducted in a 300 mL oil bath controlled by an Ace Glass Temperature Controller with a Pt thermocouple. TEM grids were obtained from Ted Pella. Carbon Type-B, 300-mesh copper grids were used with the carbon support intact. Digital TEM images were obtained using a JEOL 2000 FX instrument operating at 200 kV and fitted with a Gatan camera.
**Preparation of the primary decanethiol-capped Au nanocrystals.** The primary Au nanocrystals used in the thermal coarsening experiments were synthesized using the standard two-phase method, which is briefly summarized here to incorporate our modifications. Under vigorous stirring, an aqueous solution of HAuCl$_4$$\cdot$3H$_2$O (0.011 M, 50 mL, 0.55 mmol) was combined with a toluene solution of TOABr (0.036 M, 50 mL, 1.8 mmol), resulting in a deep-orange mixture. After the mixture was stirred for 5 min, a toluene solution of decanethiol (0.13 M, 10 mL, 1.3 mmol) was added, producing an opaque white mixture. Subsequently, an aqueous solution (10 mL) of NaBH$_4$ (30 mg, 0.8 mmol) was added rapidly, quickly turning the mixture to a dark brown as the Au nanocrystals formed. The reaction mixture was stirred an additional 4 h and then allowed to stand (≤ 10 min), whereupon the aqueous and toluene phases separated. The aqueous phase was discarded, and the volume of the toluene phase was reduced to ca. 5 mL by rotary evaporation. Immediately thereafter, EtOH (200 mL) was added to the toluene dispersion and the mixture was swirled for several minutes to precipitate the Au nanocrystals. The mixture was then allowed to stand (2-4 h), and the nanoparticles were separated by centrifugation (benchtop centrifuge). The EtOH was then decanted. The nanocrystals were redispersed in hexane (15 mL) to facilitate transfer, and dried in vacuo. (For the coarsening experiments described below, the hexane dispersion was divided into two equal aliquots, which were dried separately. Thus each coarsening experiment used half the total yield of this synthesis.) The total mass yield of decanethiol-capped Au nanocrystals was 160 mg. A simple statistical analysis of TEM images of the nanocrystals established a mean nanocrystal diameter of 1.68 nm with a standard deviation of 0.36 nm. However, the size distribution was found to be log-normal, as shown in Figure 1-37.
Conditions for measuring the coarsening kinetics of decanethiolate-capped Au nanocrystals. Newly synthesized nanoclusters (half of the above yield, or 80 mg) were redispersed in 5.00 mL diphenylmethane and placed in a 50 mL round-bottom Schlenk flask. Decanethiol (0.70 mL) was measured with a graduated pipette and added to the flask with swirling. The desired amount of TOABr was weighed to two decimal places and added to the nanoparticle solution. The resulting TOABr concentrations were calculated from the total volume of the mixtures. Total volumes were determined by adding specific masses of TOABr and 0.70 mL decanethiol to 5.00 mL diphenylmethane heating gently and measuring the volume. A linear regression was constructed from the results as shown in Figure 1-38. The concentrations (masses) of TOABr used were: 0.145M (0.50 g), 0.264 M (1.00 g), 0.362 M (1.50 g), 0.446 M (2.00 g), 0.579 M (3.00 g), 0.634 M (3.50 g), and 0.681 M (4.00 g).

The flask was capped and shaken thoroughly to mix the contents, resulting in a thick, dark
brown coating on the walls of the flask. TEM analysis prior to heating indicated that the nanoparticle dispersions were stable to aggregation at all TOABr concentrations used.

Figure 1-38. Plot of mass of TOABr added to diphenylmethane (5 ml) and decanethiol (0.7 ml) vs. total volume of solution. The linear regression obtained was used to determine the final volume for each thermal-coarsening trial. This allowed accurate determination of the salt concentration.

The flask was placed in a thermostatically controlled oil bath pre-heated to 180 ± 0.1 °C, and carefully agitated (for a maximum of 20 s) as the mixture melted to ensure homogeneity. Subsequently, the heated mixture remained unstirred. Aliquots were taken at prescribed times by removing a drop of solution with a fresh glass pipette, and immediately dispersing it into EtOH (25 mL). The EtOH dispersion was divided into two 16 × 100 mm test tubes using additional EtOH to fill the tubes, which were centrifuged for two minutes (benchtop centrifuge). The EtOH was decanted and hexane (5 mL) was added to redisperse
the nanocrystals. Specimens were prepared for TEM analysis as described below. TEM analysis was completed within 24 h of the preparation of the hexane dispersions. The collection of aliquots continued for 140-300 minutes, depending on the TOABr concentration employed. Reliable kinetic data were obtained up to the initial signs of sedimentation, which indicated gross aggregation and/or bulk-gold precipitation.

**Preparation of TEM Samples.** The hexane dispersions of nanocrystals were further diluted with an additional 2-3 mL of hexane, achieving a light pink color, to ensure a light nanocrystal coverage on the TEM grids upon deposition. One to two drops were pipetted onto a grid in air and evaporated to dryness at room temperature. All sample grids were analyzed by TEM within one hour of preparation to preclude nanocrystal ripening on the grid prior to analysis. No evidence of nanocrystal growth or agglomeration was observed during TEM analysis.

**Measurement of nanocrystal sizes and size distributions.** Digital TEM images were obtained from several locations on the sample grid. The normal bright field images were saved in a TIF format and resampled using image-processing software to increase the resolution to 400 dpi. The particle diameter distributions were measured from multiple images using Image-Pro Express software ([www.mediacy.com](http://www.mediacy.com)). A minimum of 400-1000 particles were measured for each sample, and all particles in a given image were measured to obtain an accurate ratio of small to large nanocrystals. This practice was particularly important for bimodal early-time distributions, as these samples required larger numbers of particles to be measured overall to ensure accuracy. Periodically, 2000 or more particles were measured in order to compare the mean, standard deviation, and shape of the distribution to corresponding values obtained from smaller counts. No significant difference
was detected on these occasions, indicating that the number of particles measured was sufficient to produce reliable statistics.
References


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Chapter 2

The Pathway from a Molecular Precursor to Silver Nanoparticles: The Prominent Role of Aggregative Growth
Introduction

In this study, we have elucidated the entire pathway for the growth of Ag nanoparticles from the myristate precursor [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)]. We have separately determined the kinetics of precursor disappearance and nanoparticle growth. We have directly observed a second, aggregative nucleation process. The combined results demonstrate that the growth of Ag nanoparticles under the conditions employed is dominated by aggregative processes. Finally, we argue that aggregative nucleation and growth is a more-significant component of nanoparticle formation than is generally recognized.

The two commonly invoked mechanisms for nanoparticle growth are classical nucleation and growth (the LaMer mechanism),$^{1-6}$ and Ostwald ripening.$^{7,8}$ In the LaMer or classical mechanism,$^{9-11}$ growth is initiated from crystal nuclei, and continued by molecular addition to the surfaces of the supercritical crystal seeds. Ostwald ripening requires a nanoparticle size distribution, in which the smaller nanoparticles dissolve to supply nutrient for the growth of the larger nanoparticles.$^{12}$

In the less-considered aggregative mechanism,$^{13-16}$ small primary nanocrystals aggregate and coalesce to form viable nanoparticles capable of further growth by aggregation and coalescence with additional primary nanocrystals (Scheme 1).$^{17-21}$ Aggregative growth may proceed by a second nucleation process, in which the growth-viable nanoparticles are assembled from primary nanocrystals.$^{21}$
Aggregative nucleation, aggregative growth, and Ostwald ripening – and a commonly observed sigmoidal kinetic profile. The smallest brown circles represent small, primary nanocrystals, and the larger brown circles growing nanoparticles. \( \bar{V}(t) \) is the mean nanocrystal volume at time \( t \).

Nanoparticles prepared from molecular precursors are generally presumed to have grown by the classical LaMer mechanism.\(^1\text{-}^5\) Nanoparticles prepared from smaller nanoparticles are generally presumed to have grown by Ostwald ripening.\(^7\text{-}^8\) However, we previously showed that small, primary Au nanocrystals coarsened by an aggregative nucleation-and-growth pathway.\(^21\) Here we show that Ag nanoparticles grown from a molecular precursor also form by an aggregative nucleation-and-growth mechanism.

As detailed herein, the primary evidence against classical nucleation and growth as the dominant mechanism is a comparison of the rates of precursor disappearance and nanoparticle growth. We show quantitatively that the \([\text{PPh}_3]_2\text{Ag(O}_2\text{CCH}_3\text{)}\_2\) precursor is
substantially consumed near the onset of the active growth of Ag nanoparticles. The different time scales of the two processes preclude a classical mechanism as the major component of the growth pathway. Furthermore, the observation of a second nucleation event involving small, primary Ag nanocrystallites is inconsistent with classical nucleation and growth.

Ostwald ripening is excluded as the predominant growth mechanism by the observation of pseudo-sigmoidal nanoparticle growth kinetics, bimodal nanoparticle size distributions at early times, and mature nanoparticles that are essentially all polycrystals. Additionally, we show that Ostwald ripening does occur, but only after the active-growth period. Finally, the second, aggregative nucleation process is also inconsistent with Ostwald ripening, which is not a nucleation-driven process.

Many of the arguments and mechanistic analyses employed here to establish aggregative nucleation and growth were developed in our prior study of Au nanoparticle coarsening. We show here that an aggregative mechanism may also dominate nanoparticle-growth processes that are initiated from molecular precursors. Therefore, aggregative nucleation and growth should be considered as a potentially dominant mechanism in all nanoparticle-growth procedures.
Results and Discussion

Precursor Synthesis and Characterization. Bis(triphenylphosphine)silver(I) myristate [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)] was obtained in high yield according to eq 1. To our knowledge [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)] is a new compound; however, the related bis(triphenylphosphine)silver(I) stearate was previously reported by Whitcomb and coworkers. Bis(triphenylphosphine)silver(I) myristate is a colorless solid that is soluble in organic solvents, is not light sensitive, and may be safely stored and manipulated under ambient air at room temperature for at least 2 years.

\[
2\text{PPh}_3 + \text{Ag}(\text{O}_2\text{CC}_{13}\text{H}_{27}) \rightarrow (\text{PPh}_3)_2\text{Ag}(\text{O}_2\text{CC}_{13}\text{H}_{27}) \quad (1)
\]

The molecular structure of [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)] determined crystallographically is shown in Figure 2-1. It is isostructural with the analog synthesized by Whitcomb and coworkers. The molecular unit is mononuclear with a four-coordinate silver atom in a distorted-tetrahedral coordination environment. The myristate ligand is bidentate. Key bond distances and angles are summarized in the caption to Figure 2-1. The crystallographic data are recorded in Table 2-1.
Figure 2-1. A thermal-ellipsoid plot of [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)]. Hydrogen atoms and one of the two unique molecules are omitted for clarity. Selected distances (Å): Ag(1)-P(1), 2.4115(10); Ag(1)-P(2), 2.4292 (10); Ag(1)-O(1), 2.384(3); Ag(1)-O(2), 2.497(3). Selected angles (deg): O(1)-Ag(1)-P(1), 114.72(7); O(1)-Ag(1)-P(2), 104.88(7); P(1)-Ag(1)-P(2), 134.22(4); O(1)-Ag(1)-O(2), 53.86(9); P(1)-Ag(1)-O(2), 110.60(7); P(2)-Ag(1)-O(2), 110.94(7).
Table 2-1. Crystal data and structure refinement for [(PPh₃)₂Ag(O₂CC₁₃H₂₇)].

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<tr>
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The low-temperature $^{31}$P{H} NMR spectrum of $\left[(\text{PPh}_3)_2\text{Ag(O}_2\text{C}_{13}\text{H}_{27})\right]$ in $d_6$-acetone (-80 °C) consisted of two doublets (Figure 2-2), corresponding to two ($^{107}\text{Ag}$ and $^{109}\text{Ag}$) isotopomers in near-equal amounts. The abundant isotopes of Ag are $^{107}\text{Ag}$ (51.82%) and $^{109}\text{Ag}$ (48.18%), and both have nuclear spins of $I = \frac{1}{2}$. Two doublets with very similar chemical shifts of 8.63 and 8.64 ppm, respectively, were thus observed. The P–Ag coupling constants were also similar: $^1J\left(P, ^{109}\text{Ag}\right) = 471.98$ Hz, and $^1J\left(P, ^{107}\text{Ag}\right) = 414.13$ Hz. The ratio $^1J\left(^{107}\text{Ag}^{31}\text{P}\right) : ^1J\left(^{109}\text{Ag}^{31}\text{P}\right)$ was 0.877, which agrees with the ratio of gyromagnetic ratios, $\gamma(^{107}\text{Ag}) : \gamma(^{109}\text{Ag}) = 0.870$.\textsuperscript{34-36}

$^{31}$P{H} NMR spectra recorded at various temperatures between -80 and 25 °C are shown in Figure 2-2. The two doublets observed at -80 °C coalesced into a single resonance at -40 °C, and further sharpened at room temperature. Similar coalescence behavior was observed previously for other silver-phosphine complexes,\textsuperscript{34,37} and was attributed to a dissociative equilibrium that exchanges bound and free phosphine ligands and therefore collapses the P–Ag $J$ coupling.
Silver Nanoparticle Formation. Silver nanoparticles were produced by reaction of the silver precursor and AIBN in solution (130 °C) in the presence of poly(1-hexadecene)$_{0.67}$ - co- (1-vinylpyrrollidone)$_{0.33}$ (PHD-co-PVP)$_{38,39}$ as a polymer stabilizer. Nanoparticle formation was monitored by UV-visible spectroscopy. A peak emerged in the extinction spectrum (Figure 2-3) at $\lambda_{\text{max}} = 420$ nm, which shifted towards $\lambda_{\text{max}} = 409$ nm and grew in intensity over the course of the growth period (80-90 min). This peak is consistent with the surface-plasmon resonance of Ag nanoparticles in the size range of 1-15 nm.$^{40-42}$ TEM images confirmed the formation of small nanoparticles at early times, which evolved into larger nanoparticles as growth proceeded (see below). Energy-dispersive X-ray spectroscopy on the nanoparticles confirmed their elemental-Ag composition (Figure 2-4). Lattice spacings measured from HRTEM images (0.25 ± 0.06 nm, Figure 2-5) were consistent with $d_{111}$ in fcc Ag (0.24 nm according to ICDD-PDF #01-071-3762).
Figure 2-3. UV-visible extinction spectra of Ag nanoparticles after background subtraction (see the Experimental section). The spectra were collected at various times during a growth trial as indicated in the inset.
Figure 2-4. An energy-dispersive X-ray spectrum of Ag nanoparticles formed by eq 2. The data were collected using a JEOL 2000FX TEM. The Cu signals are due to the TEM sample grid.

Figure 2-5. An HRTEM image of a polycrystalline Ag nanoparticle showing a $d_{111}$ lattice spacing of 0.25 ± 0.06 nm. The scale bar is 5 nm.
Reaction Monitoring. The phosphorus byproduct of Ag-nanoparticle formation was identified by $^{31}$P{$^1$H} NMR monitoring. Spectra obtained over the course of the reaction revealed the disappearance of the Ag-precursor resonance at 8.7 ppm with the appearance of a product resonance at 26.2 ppm (Figure 2-6). The product resonance was shown to correspond to the phosphine oxide Ph$_3$P=O by independent measurement of the spectrum of authentic Ph$_3$P=O under identical conditions. Additionally, authentic Ph$_3$P=O was spiked into a reaction mixture, upon which the intensity of the product resonance at 26.2 ppm was increased.

![31P NMR spectra taken at various times during the decomposition of [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_2$)$_2$] at 130 °C. The precursor resonance (8.7 ppm) disappears as the product Ph$_3$P=O resonance (26.2 ppm) appears.](image)

**Figure 2-6.** $^{31}$P{$^1$H} NMR spectra taken at various times during the decomposition of [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_2$)$_2$] at 130 °C. The precursor resonance (8.7 ppm) disappears as the product Ph$_3$P=O resonance (26.2 ppm) appears.
The organic byproduct of the reaction was established by electrospray-ionization mass spectrometry (ESI-MS) and $^{13}$C{$_1^1$H} NMR. To obtain appropriate specimens for these analyses, the Ag-generating reaction described above was conducted on a larger scale and in the absence of the PHD-co-PVP polymer stabilizer. The reaction mixture was decanted, the solvent was evaporated, and the residue was analyzed. The base peak in the ESI-MS (Figure 7) corresponded to $m/z = 279$ amu. The $^{13}$C{$_1^1$H} NMR spectrum (Figure 2-8) contained the characteristic resonances for the hydrocarbon chain for the myristyl group, and resonances assigned to cyano (CN, 122.0 ppm) and carbonyl (CO, 180.7 ppm) carbon atoms. The results indicated that the organic byproduct was compound I (MW = 279 g/mol, eq 2), resulting from the coupling of fragments derived from the myristate ligand and AIBN. The reaction stoichiometry in eq 2 was therefore identified.
Figure 2-7. An ESI-MS spectrum collected from the byproducts of eq 2. The base peak at 279 amu corresponds to byproduct I in eq 2.

Figure 2-8. A $^{13}$C{$^{1}$H} NMR spectrum (in acetone-$d_{6}$) collected from the byproducts of eq 2. The major resonances in the spectrum pertain to Ph$_3$P=O and compound I. The cyano (CN) resonance at 122.0 ppm and the carbonyl (CO) resonance at 180.7 ppm are assigned to I.
As a control experiment, Ag nanoparticle growth was conducted as described in the section above, except in a nitrogen-purged solution and under a nitrogen atmosphere, rather than under ambient air. The progress of nanoparticle growth, which was monitored by UV-visible spectroscopy, was significantly inhibited under these conditions. After a growth period of 50 minutes, the Ag-nanoparticle plasmon feature was extremely broad and scarcely detectable, establishing that the nanoparticle mean size was well below 3 nm, a size achieved under normal conditions within 3-5 min (see below). We attributed this inhibition to the lack of the O$_2$ necessary to support eq 2.

A kinetics study of precursor disappearance according to eq 2 was conducted at 130.0 ± 0.1 °C, under air and with a 12-fold excess of AIBN. $^{31}$P{$^1$H} NMR data like those in Figure 6 were integrated to provide quantitative measures of precursor remaining and Ph$_3$P=O product formed (the spectra shown in Figure 2-6 constitute a partial set). Precursor disappearance was plotted as the natural log of the integrated precursor resonance ($^{31}$P$_{prec}$) divided by the total integrated area of the precursor and product resonances ($^{31}$P$_{prec}$ + $^{31}$P$_{prod}$) vs. time, ln[$(^{31}$P$_{prec})/(^{31}$P$_{prec}$ + $^{31}$P$_{prod}$)] vs. $t$ (Figure 2-9). The plot was linear over approximately 3 half-lives, establishing pseudo first-order kinetics for the disappearance of [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)]. A rate constant of 0.190 ± 0.022 min$^{-1}$ was obtained, yielding a half-life of 3.65 ± 0.42 min. This quantitative value will be used below in the determination of the mechanism of nanoparticle growth, and will rule out a classical, LaMer-type mechanism as the predominant nanoparticle-growth mechanism.
Figure 2-9. Plot of the natural log of the integrated $^{31}$P-NMR precursor intensity divided by the total integrated $^{31}$P-NMR intensity vs. time for [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)] disappearance by eq 2.

**Early-time Particle-Growth Monitoring.** Nanoparticle growth was monitored by removing aliquots for TEM analysis from kinetics runs conducted at 130.0 ± 0.1 ºC (eq 2). A distribution of small nanoparticles having diameters of 1.8 ± 0.6 nm was observed to emerge at reaction times as short as 3-4 min (Figure 2-10a). We refer to these small nanoparticles as primary nanocrystals. TEM images of aliquots taken just a few minutes later revealed a population of distinctly larger nanoparticles interspersed with the primary nanocrystals (Figure 2-10b); that is, the crystal-size distribution (CSD) evolved from asymptotic to bimodal (Figure 2-11). We note that contrast limitations in the images of the bimodal distributions precluded a complete count of the remaining primary nanocrystals, which were difficult to discern in the presence of the larger nanoparticles. In time, the primary
nanocrystals disappeared as the larger nanoparticles continued to grow, reaching a mean size of $7.3 \pm 0.7$ nm after 50-60 min (Figure 2-10c).

**Figure 2-10.** TEM images obtained at various stages of Ag-nanoparticle growth. (a) After 3 min, (b) after 5 min, and (c) after 55 min.

![Figure 2-10](image)

**Figure 2-11.** CSDs determined in a Ag-nanoparticle growth trial at 3 min (black), 5 min (red), and 7 min (green). The plots show the evolution of the CSDs from asymptotic to bimodal. The fraction $F$ of the nanoparticles in a given volume bin is plotted against nanoparticle volume.
HRTEM studies were undertaken to determine the crystallinity of the larger nanoparticles. Images were obtained of both smaller (but not primary) nanoparticles from early times, and larger nanoparticles from later times (Figure 2-5). The vast majority of the nanoparticles examined were polycrystalline, as shown in Figure 2-5, which is consistent with an aggregative growth process involving aggregation and coalescence of primary nanocrystals.6,16,21,31,32,44,45

**Determination of the Aggregative-Nucleation Function.** A more-extensive set of CSDs obtained from a kinetics trial is given in Figure 2-12. The bimodality observed in the early-time CSDs is primary evidence of nanoparticle aggregation.17-21,26-28 We have previously found that aggregative growth may be a nucleation-driven process, requiring the formation of a critical aggregate of primary nanocrystals to initiate further aggregative growth. Because the primary nanocrystals resulted from a classical nucleation and growth, the aggregative-nucleation process constitutes a second nucleation event.
Figure 2-12. An extensive series of CSDs determined at various times (inset) in an Ag-nanoparticle-growth trial, including the three plots shown in Figure 8. The fraction $F$ of nanoparticles in a given volume bin is plotted against nanoparticle volume.

We and others have shown that a peak emerges in the CSD at the critical-nucleus size (evident at 5 min in Figure 2-12), which subsequently shifts to progressively larger size. This emergent peak results from a burst of nucleation, corresponding to a rapidly increasing nucleation rate.\textsuperscript{28,46-50} In aggregative growth, the nucleation corresponds to the formation of critical-sized aggregates, which coalesce and subsequently grow by addition of primary nanocrystals.\textsuperscript{21} The nucleation rate then falls off as growth ensues. Consequently, the nucleation function – the time dependence of the aggregative-nucleation rate $\Gamma(t)$ – first rises, passes through a maximum $\Gamma_{\text{max}}$, and then decays (see below).

The critical-aggregate size, expressed as a volume $V_{\text{crit}}$, was revealed by Figure 2-9 (5 min) to be $27.5 \pm 2.5 \text{ nm}^3$, or 10 (1.7-nm-diameter) primary nanocrystals, corresponding to an effective diameter of 3.9 nm for the coalesced critical aggregate. This $V_{\text{crit}}$ value was
used\textsuperscript{21} to construct the nucleation function as follows. The fraction $F_{\text{crit}}$ of nanoparticles in the CSDs having the critical size $V_{\text{crit}}$ was plotted vs. time (Figure 2-13). The $F_{\text{crit}}$ data were fitted with the Gaussian profile in eq 3, where $t$ is time, $\Delta t_n$ is the $2\sigma$ width of the Gaussian, $\tau_n$ is the time at the Gaussian maximum, and $A$ is the area under the Gaussian (all in min).

The Gaussian was scaled as the nucleation function $\Gamma(t)$ by setting $A$ (in eq 3) equal to $N$, the number of critical aggregates formed, and by calculating $\Gamma_{\text{max}}$ from eq 4.\textsuperscript{21} The quantity $N$ was estimated from the mean final nanoparticle volume and the total amount of Ag as previously described.\textsuperscript{21} The time at the maximum aggregative-nucleation rate $\Gamma_{\text{max}}$ and the width of the time window for aggregative nucleation were determined to be $\tau_n = 7.50 \pm 0.29$ min and $\Delta t_n = 2.80 \pm 0.32$ min, respectively, by the eq-3 fit. These quantities provide measures of the time scale for aggregative nucleation, and are used below to characterize the growth mechanism.

\[
F_{\text{crit}}(t) = \frac{A}{\Delta t_n \sqrt{2\pi}} \exp \left[ -\frac{2(t - \tau_n)^2}{\Delta t_n^2} \right] \tag{3}
\]

\[
\Gamma_{\text{max}} = \frac{N}{\Delta t_n \sqrt{\pi} 2^{\frac{1}{2}}} \tag{4}
\]
Figure 2-13. The aggregative-nucleation function (Gaussian fit) for Ag-nanoparticle growth under the conditions described in the text. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma(t)$, respectively (see text).

**Measurement of Particle-Growth Kinetics.** The time evolution of the Ag nanoparticle mean volume was followed by both TEM and UV-visible spectroscopy. However, because the TEM CSDs were obtained by counting only 400-750 nanoparticles, whereas the UV-visible analyses effectively measured the entire nanoparticle populations, the UV-visible data were considered to provide a statistically more-reliable measure of the nanoparticle mean size. Consequently, the nanoparticle-growth kinetic profiles were composed primarily of UV-visible data.

Calibration plots were constructed to relate TEM-determined mean diameters with the height of the plasmon resonance in the corresponding UV-visible spectra. These plots used the TEM and UV-visible data collected from five separate kinetics trials. As described in the Experimental section, the plasmon-feature height was extracted from the UV-visible
extinction spectra by background subtraction and Lorentzian fitting. The plots of TEM mean diameter (in nm) vs. plasmon-feature height (in absorbance units) were empirically linear (Figure 2-14). The slopes and intercepts extracted by least-squares fitting were averaged to give eq 5, where \( \overline{d} \) is the mean diameter and \( A \) is absorbance (extinction). Mean nanoparticle diameters determined from the UV-visible data with eq 5 were converted to mean volumes for the kinetic analyses by assuming spherical morphologies.

\[
\overline{d} \text{ (in nm)} = (5.41 \pm 0.37)A \text{ (in abs. units)} + (3.34 \pm 0.35) \quad (5)
\]

**Figure 2-14.** A plot of mean Ag-nanoparticle diameter determined from TEM images vs. the surface-plasmon absorbance in the corresponding UV-visible spectrum. The plasmon absorbance was obtained by fitting and background subtraction as described in the Experimental section. The data plotted here were obtained from a single kinetics trial. The slope and intercept were extracted by linear least-squares fitting. The slope and intercept values from five such sets of data were averaged to give eq 5 (see text).
A representative kinetic profile for Ag-nanoparticle growth is given in Figure 2-15. The data are plotted as $\bar{V}(t)/\bar{V}_{\text{lim}}$ vs. time, where $\bar{V}(t)$ is the mean nanoparticle volume and $\bar{V}_{\text{lim}}$ is the limiting mean volume at the end of the active-growth period (see below; $1/\bar{V}_{\text{lim}}$ is a merely scaling factor). Figure 2-15 includes both TEM and UV-visible data; however, the UV-vis data were used in the kinetic fits discussed below, except for the time points at which the mean nanoparticle diameters were below 3 nm. We found that nanoparticles having diameters below about 3 nm did not produce readily discernible plasmonic features. Thus the $\bar{V}(t)/\bar{V}_{\text{lim}}$ data for time points earlier than 5 minutes were determined from TEM data.

As revealed by Figure 2-15, the kinetic plots exhibited a pseudo-sigmoidal profile, which is further analyzed below.

**Figure 2-15.** Kinetic data and the eq-6 fit (red curve) for Ag-nanoparticle growth. The black curve plots the first term only from the eq-6 fit. $\bar{V}(t)$ is the time-dependent nanoparticle mean volume, and $\bar{V}_{\text{lim}}$ is the mean volume at the end of active growth (at 60 min).
Nanoparticle-growth kinetics often exhibit a sigmoidal profile resembling that in Scheme 1.\textsuperscript{13,22-25,30,51-53} The initial induction period is associated with the nucleation process, which is followed by a rapid nanoparticle-size increase associated with the active-growth regime. At the end of active growth a plateau occurs in the kinetic profile, until the onset of Ostwald ripening. In our case, aggregative nucleation began so early (3 min; see Figure 2-10) that the initial induction period was not observed. Furthermore, Ostwald ripening began shortly after the end of the aggregative-growth regime, such that the final plateau extended for only about 7 min prior to the onset of further growth by Ostwald ripening (see below). Consequently, we describe the kinetic profile as pseudo-sigmoidal.

We\textsuperscript{21} and others\textsuperscript{53} have shown that sigmoidal nanoparticle-growth profiles are in some cases well fit by a KJMA model. However, we found a simple KJMA equation unable to fit the rising slope in the Figure 2-15 data at later times. We attributed this late-time nanoparticle growth to Ostwald ripening, which is known to produce a linear increase in mean particle volume with time.\textsuperscript{12,54-56} Additionally, the conditions favorable to Ostwald ripening require the depletion of the growth nutrient,\textsuperscript{51,57-60} which in this case was primary Ag nanocrystals. Consequently, one expects the onset of Ostwald ripening after the conclusion of the active-growth regime.

The Figure 2-15 data were fit by a modified KJMA expression (eq 6) to determine the time for the onset of Ostwald ripening ($\tau_{\text{OR}}$). Equation 6 consists of two terms, the first of which is a standard KJMA term to fit nucleation and active growth, where $k_g$ (min$^{-1}$) is a rate parameter and $n$ the Avrami exponent.\textsuperscript{21} The second term provides a linear increase in mean volume to account for Ostwald ripening.\textsuperscript{54-56} The rate parameter for Ostwald ripening $k_{\text{OR}}$
(min\(^{-1}\)) is multiplied by a logistic, “turn-on” function to activate Ostwald ripening at a time \(\tau_{OR}\) (min). The time width \(w\) of the turn-on function was arbitrarily chosen to be 2 min. Thus, the fitting parameters were \(k_g\), \(n\), \(k_{OR}\), and \(\tau_{OR}\), with the fitted value of \(\tau_{OR}\) being of primary interest.

\[
\frac{\bar{V}(t)/\bar{V}_{lim}}{\bar{V}_{lim}} = \left(1 - \exp\left(-k_g t\right)^n\right) + \left[\frac{\left(t-\tau_{OR}\right)}{1+\exp\left(-2w(t-\tau_{OR})\right)}\right]^{k_{OR}} \tag{6}
\]

Two curves are plotted in Figure 2-15. The red curve is the full eq-6 fit, and the black curve plots the first, KJMA term only. The primary difference is that the red curve tracks the Ostwald ripening at later times, whereas the black curve levels off at the conclusion of the active (aggregative) growth regime. The value of \(\tau_{OR}\) determined from the eq-6 fit was 57.9 ± 3.4 min, indicating that Ostwald ripening began at that time.

We next sought to determine the start time for Ostwald ripening by a second quantitative measure. Prior studies elsewhere have shown that the CSD narrows during the active-growth regime,\(^{51,57,60}\) including by aggregative growth,\(^{18}\) and reaches its minimum value at the conclusion of active, nutrient-supported growth. The nanoparticle mean size then remains nearly constant for a period as the CSD begins to spontaneously broaden,\(^{51,57,60,61}\) initiating Ostwald ripening, which is facilitated by a broadened CSD. Therefore, after a rest period the mean size begins to increase by Ostwald ripening. Such a rest period is evident in Figure 2-15 in the range of approximately 53-60 min. Conventional Ostwald ripening progressively broadens the CSD, and so the onset of this broadening provides a second measure of the onset time for Ostwald ripening.\(^{51,57,60}\)
The relative standard deviation in the Ag-nanoparticle CSD during a growth trial is plotted in Figure 2-16. The CSD was observed to initially narrow, and achieve a minimum value at 53 min. Subsequently, the CSD rebroadened. The onset of this rebroadening was estimated from the Figure-16 data to be $60 \pm 5$ min, in remarkable agreement with the value of $\tau_{OR} = 57.9 \pm 3.4$ min (see above). Consequently, the onset of Ostwald ripening was determined to be 58-60 min by two independent quantitative measures.

Figure 2-16. A plot of relative standard deviation in the nanoparticle CSD vs. time. The plot passes through a minimum before starting to re-broaden, indicating the end of aggregative growth and the onset of Ostwald ripening. The relative standard deviation is the standard deviation in the diameter divided by the nanoparticle mean diameter.

Precursor-Decomposition Chemistry. The Ag-generating reaction in eq 2 was developed by us empirically. Silver carboxylates decompose thermally to elemental Ag, and have been used in photothermographic applications$^{62-65}$ and to deposit Ag films by chemical
vapor deposition (CVD)\textsuperscript{66-69} and atomic layer deposition (ALD).\textsuperscript{70} Prior reports of Ag-nanoparticle formation from Ag-carboxylate precursors also exist.\textsuperscript{71,72}

We found that the precursor [(PPh\textsubscript{3})\textsubscript{2}Ag(O\textsubscript{2}CC\textsubscript{13}H\textsubscript{27})] decomposed only very slowly at 130 °C in o-dichlorobenzene solvent and in the presence of the polymer stabilizer. However, at 150 °C under the same conditions, the decomposition was extremely rapid and the resulting Ag nanoparticles exhibited broad size distributions. Several studies have suggested that Ag carboxylates decompose by radical pathways,\textsuperscript{68,73,74} and so we attempted to accelerate Ag-nanoparticle formation at 130 °C by the addition of the radical initiator AIBN.

In our initial efforts we added small, sub-stoichiometric quantities of AIBN to the precursor mixture. Some Ag nanoparticles were readily generated at 130 °C, but NMR analysis revealed large amounts of unreacted [(PPh\textsubscript{3})\textsubscript{2}Ag(O\textsubscript{2}CC\textsubscript{13}H\textsubscript{27})], even after extended periods. We surmised that the early termination of precursor decomposition indicated a stoichiometric role for AIBN. We ultimately determined that an AIBN/precursor molar ratio of about 6 was necessary for complete conversion to elemental Ag, and elucidated the eq-2 stoichiometry as described in the previously.

The reaction pathway for eq 2 is not immediately apparent. A C-O bond in the myristate ligand is cleaved, and the remaining fragment is united with the alkyl substituent derived from AIBN in byproduct I (eq 2). Both Ph\textsubscript{3}P ligands are converted to the oxide Ph\textsubscript{3}P=O. Hints to a possible pathway are provided in a study of the gas-phase thermolysis of [(n-Bu\textsubscript{3}P)\textsubscript{2}Ag(O\textsubscript{2}CCF\textsubscript{3})] by Kohse-Höinghaus and coworkers.\textsuperscript{68} The gas-phase decomposition was monitored by mass spectrometry, and one of the predominant fragments observed corresponded to [(n-Bu\textsubscript{3}P)\textsubscript{2}Ag(O)]\textsuperscript{+} and/or [(n-Bu\textsubscript{3}P)(n-Bu\textsubscript{3}P=O)Ag]\textsuperscript{+} (m/z = 527). That finding suggests to us the pathway outlined in Scheme 2-2.
Scheme 2-2. A proposed reaction pathway for precursor decomposition according to eq 2 (see text).
In Scheme 2-2, we propose thermal decomposition of AIBN in an initial step, generating $\text{Me}_2(\text{CN})\text{C}^\cdot$ radicals. Radical attack at the myristate carbonyl carbon atom would produce byproduct I and $[(\text{Ph}_3\text{P})_2\text{Ag(O)}]^\cdot$ by ligand fragmentation. The 12-fold excess of AIBN is presumably required because the $\text{Me}_2(\text{CN})\text{C}^\cdot$ radicals may be lost to reactions with the solvent or in other ways, and only a fraction survives to attack the precursor. The $[(\text{Ph}_3\text{P})_2\text{Ag(O)}]^\cdot$ intermediate may rearrange to $[(\text{Ph}_3\text{P})(\text{Ph}_3\text{P}=\text{O})\text{Ag}]^\cdot$, and re-oxidize to $[(\text{Ph}_3\text{P})(\text{Ph}_3\text{P}=\text{O})\text{Ag(O)}]^\cdot$. We note that eq 2 is conducted under ambient air, and fails to progress when conducted under O$_2$-free conditions (see above). A final rearrangement and ligand dissociation would liberate two equivalents of Ph$_3$P=O and an Ag atom. Scheme 2 accounts for the stoichiometric consumption of AIBN and the necessity of O$_2$, rationalizes all eq-2 reaction products, and is consistent with the available precedent.$^{68}$

**Elucidation of the Nanoparticle-Growth Pathway.** The kinetic results for Ag-nanoparticle formation described above establish that classical nucleation and growth, aggregative nucleation and growth, and Ostwald ripening are largely consecutive processes, separated in time from one another. Classical nucleation and growth occurs early, on a time scale that is measured by the half life for precursor decomposition ($t_{1/2} = 3.65 \pm 0.42$ min). After the rapid, initial formation of small, primary nanocrystals, larger nanoparticles first appear after about 3-4 min (Figure 2-10a), at which time the $[(\text{PPh}_3)_2\text{Ag(O}_2\text{CC}_{13}\text{H}_{27})]$ precursor is half consumed. Figure 2-13 shows that when the (aggregative) nucleation rate reaches a maximum ($\tau_n = 7.50 \pm 0.29$ min), the precursor is 75% consumed. Figure 2-15 reveals that the active growth period extends to 58 mins. Thus, 4 half lives of precursor decomposition (14.6 min), at which point 94% of the precursor has been consumed, occurs within the first 25% of the growth period. Because of the early time scale for precursor
decomposition, the LaMer or classical mechanism accounts well for the initial burst of small, primary Ag nanocrystals, but is temporally inconsistent with the extended active-growth regime.

One must next consider if Ostwald ripening can account for the active-growth regime extending to 58 minutes. However, the observations of pseudo-sigmoidal growth kinetics, bimodal CSDs at early times, polycrystalline mature nanoparticles, and a second, nonclassical nucleation process are all inconsistent with Ostwald ripening. As noted above, the increase in the mean nanoparticle volume by Ostwald ripening should be linear, not sigmoidal, in time. As we have discussed extensively previously, Ostwald ripening cannot generate a bifurcated (bimodal) CSD unless a discontinuity in the growth rate occurs at a critical nanoparticle size, resulting from substrate-nanoparticle strain or a nanoparticle morphology transition. No such special circumstance exists here. Ostwald ripening of small, primary nanocrystals should produce mature nanoparticles that are single crystals rather than polycrystals. Finally, Ostwald ripening is not a nucleation-driven process, and so cannot account for the nucleation behavior evident in Figures 12 and 13. Instead, each of these observations is theoretically and experimentally consistent with an aggregative-growth mechanism.

We assert that Ostwald ripening begins after the conclusion of the active-growth period at 58 min (see Figure 2-15). As described above, two independent measures place the onset of Ostwald ripening at this time: the fitted τ_{OR} value of 57.9 ± 3.4 min from eq 6, and the time of CSD rebroadening at 60 ± 5 min from Figure 16. Consequently, classical nucleation and growth, aggregative nucleation and growth, and Ostwald ripening all contribute to Ag-nanoparticle growth under the conditions employed, but in different time regimes. The
regime of greatest nanoparticle growth is governed by aggregative processes. For synthetic purposes, one would ideally find conditions that eliminate the late-time Ostwald ripening such that the final nanoparticle mean size and size distribution would be fixed at and controlled by the conclusion of the aggregative-growth regime.

The Participation of Aggregative Processes in Nanoparticle Growth. Although not yet widely appreciated, the contribution of aggregative processes to particle and nanoparticle growth has been recognized at least since the work of Matijević, Turkevich, and Zukoski. Aggregation is also an intrinsic component of growth by oriented attachment. Theoretical studies by Zukoski and coworkers show small nanocrystals to be unstable with respect to aggregation on time scales shorter than those for classical growth. Finke and coworkers have developed kinetics models that incorporate aggregative steps into nanoparticle-growth mechanisms. More recently, Alivisatos and coworkers have directly observed nanoparticle aggregation and coalescence in the TEM. Evidence for aggregative growth includes the observation of particles composed of smaller primary nanocrystals and decreasing particle number densities with time. Indeed, decreasing particle number densities have been found in the growth of LaMer sulfur sols, arguing for the participation of aggregative processes even in this classic case.

Two recent studies are particularly relevant to the results presented here. Kraehnert, Emmerling, and coworkers studied the nucleation and growth of Au nanoparticles by reduction of tetrachloroauric acid, with monitoring by small-angle X-ray scattering and X-ray absorption near-edge spectroscopy. The results provide strong evidence for the participation of aggregative processes. When the comparatively mild reducing agent citrate is employed, the time regimes for the chemical reduction, classical nucleation and growth,
and aggregative growth overlap significantly.\textsuperscript{44} However, when the stronger reducing agent sodium borohydride is employed, the reduction and classical nucleation and growth, resulting in small, primary nanocrystals (of size $\sim 1$ nm) is rapid, and is subsequently followed by a separate aggregative-growth regime.\textsuperscript{45} The latter case parallels the findings reported here for Ag nanoparticles.

An important study of Ag-nanoparticle formation was reported by Van Hyning, Klemperer, and Zukoski several years ago.\textsuperscript{14} They monitored nanoparticle growth by the borohydride reduction of Ag ions in aqueous solution. Their results foreshadowed those obtained later by Kraehnert, Emmerling, and coworkers for the borohydride reduction of tetrachloroauric acid.\textsuperscript{45} Van Hyning, Klemperer, and Zukoski found that the concentration of Ag ions dropped by two orders of magnitude within the first 5 s of reaction, producing primary Ag nanocrystals having dimensions of about 2.5 nm. Subsequently, Ag-nanoparticle growth occurred over the next 20-50 minutes by aggregative processes involving the primary nanocrystals. Our results mimic those of Van Hyning, Klemperer, and Zukoski, although we have formed Ag nanoparticles from a molecular precursor and by eq 2, and have used general conditions that are quite different than those they employed.\textsuperscript{14}

We demonstrated here and previously\textsuperscript{21} that aggregative growth may be nucleation driven, and that the nucleation function for this nonclassical process may be experimentally determined (see Figure 2-13). The nucleation function is the key to achieving control over final nanoparticle mean sizes and size distributions. We showed previously that the time width of the nucleation function is strongly correlated with the size distribution, and that the width of the function may be purposely varied by a salt additive.\textsuperscript{21} Furthermore, the area under the nucleation function is the number of critical aggregates formed, which is equal to
the number of growth-viable nanoparticles, and thus the final number of nanoparticles. We showed previously that this area is strongly correlated with the final nanoparticle mean size.\textsuperscript{21} Thus, important synthetic advances will be realized when the height and width of the aggregative-nucleation function can be systematically controlled.

**Conclusion**

The results reported here establish that the pathway for the growth of Ag nanoparticles from [(PPh\(_3\))\(_2\)Ag(O\(_2\)CC\(_{13}H\(_{27}\))] according to eq 2 consists of four processes: precursor decomposition, classical or LaMer nucleation and growth, aggregative nucleation and growth, and Ostwald ripening. The three nanoparticle growth and ripening processes occur in consecutive time regimes. Precursor decomposition and classical nucleation and growth occur concurrently in the first regime. Although nanoparticles prepared from molecular precursors are generally considered to have grown by the LaMer mechanism, and nanoparticles prepared from smaller nanocrystals to have grown by Ostwald ripening, the results here and elsewhere\textsuperscript{13,14,21-25,44,45} establish that aggregative growth can contribute prominently in both cases. Indeed, Ag-nanoparticle growth according to eq 2 is dominated by aggregative processes. Therefore, aggregative growth should be considered a potential contributing mechanism in all nanoparticle-forming reactions.
Experimental Section

General methods and materials. Poly(1-hexadecene)_{0.67} - co- (1-vinylpyrrolidone)_{0.33}, myristic acid (99%), silver nitrate (99%), benzene (99%), 1,2- dichlorobenzene (99%), and cyclohexane (99%) were purchased from Aldrich and used as received. Azoisobutyronitrile (AIBN) was purchased from Aldrich and purified by recrystallization from hot ethanol. All reactions were conducted in the ambient atmosphere. Mass spectrometry was performed using a Bruker Maxis Q-TOF mass spectrometer. $^{31}$P NMR spectra were collected on a Varian INOVA-300 spectrometer at 121 MHz, and $^{13}$C{$^1$H}NMR spectra on a Varian INOVA-600 spectrometer at 150 MHz. TEM images were recorded using a JEOL 2000FX microscope operating at 200kV. High-resolution TEM (HRTEM) images were recorded on a JEOL JEM-2100F microscope operating at 200kV. UV-visible spectra were recorded on a Varian Carey 1E spectrophotometer at room temperature. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of silver myristate (C$_{13}$H$_{27}$CO$_2$Ag). Myristic acid (9.83 g, 43.0 mmol) was dissolved in acetone (250 ml) in a 500 ml Erlenmeyer flask. To the stirring myristic acid solution, silver nitrate (7.31 g, 43.0 mmol) dissolved in 3:1 v/v water/acetone mixture (200 ml) was added, resulting in immediate precipitation. The suspension was filtered and the precipitate washed with water (ca. 200 ml), followed by acetone (ca. 100 ml). The solid was dried in vacuo at 100 ºC for 72 hours. Yield: 8.54 g, 25.5 mmol, 85%.

Anal. Caled for C$_{13}$H$_{27}$CO$_2$Ag: C, 50.15; H, 8.11. Found, C, 49.52; H, 8.10; N, < 0.5. All values are given as percentages.
Synthesis of bis(triphenylphosphine)silver(I) myristate [(PPh₃)₂Ag(O₂CC₁₃H₂₇)].

Silver myristate (6.0 g, 18 mmol) was added to benzene (200 ml) containing dissolved triphenylphosphine (11.0 g, 42.0 mmol) in a 500 ml-round-bottom flask. The stirred mixture was refluxed for one hour, resulting in the dissolution of the silver myristate. While it was still warm, the solution was transferred to a 500-ml beaker, covered, and left to cool. After the beaker was allowed to stand (24 h), colorless spindle-like crystals appeared. The crystals were separated from the supernatant by filtration, washed with acetone (25 ml) and dried in vacuo. Yield: 11.28 g, 13.12 mmol, 73 %; mp 111-113 ºC.

Anal. Calcd for [(PPh₃)₂Ag(O₂CC₁₃H₂₇)]: C, 69.85; H, 6.88; P, 7.20. Found, C, 69.76; H, 6.45; P, 7.37; N, < 0.5. All values are given as percentages. ¹H NMR (300 MHz, d₆-acetone, δ): 7.3-7.5 (m, 30 H, C₆H₅), 2.1 (t, 2H, CH₂), 1.5 (m, 2H, CH₂), 1.3 (m, 20H, CH₂), 0.9 (t, 3H, CH₃). ³¹P{¹H} NMR (121 MHz, d₆-acetone, -80 ºC, ppm): 8.64 (d, ¹J (P,¹⁰⁹Ag) = 471.98 Hz), 8.63 (¹J (P,¹⁰⁷Ag) = 414.13 Hz). ³¹P{¹H} NMR (121 MHz, d₆-acetone, 25 ºC, ppm): 8.7 (s).

Collection of kinetic data for silver nanoparticle growth. In a typical trial, bis(triphenylphosphine)silver(I) myristate (0.044 g, 0.051 mmol) and AIBN (0.05 g, 0.3 mmol) were dissolved in 4% w/w poly(1-hexadecene)₀.₆₇ - co- (1-vinylpyrrolidone)₀.₃₃ in 1,2-dichlorobenzene (10 ml) in a 50 ml round bottom flask under ambient air. The stirred mixture was heated at 130.0 ± 0.1 ºC in a 300-ml oil bath connected to an Ace Glass temperature controller. Aliquots were taken at specific time intervals by removing approximately 0.5 ml of the solution with a fresh glass pipette and dispersing the aliquot in methanol (5 ml). The resulting dispersion was centrifuged for ca. 2 minutes, the supernatant discarded, and the precipitate redispersed in toluene (4 ml). Collection of aliquots continued
for 70 – 100 min. Reliable kinetic data could be obtained up to the initial signs of sedimentation, which was indicated by the appearance of a brown film on the sides of the flask.

**Collection of precursor-disappearance data.** Trials were run to monitor the disappearance of the precursor as a function of time. For each, a nanoparticle-growth mixture was prepared and heated as described above. Aliquots (1.0 ml) of the heated mixture were taken at specific time intervals and dispersed in ice-cold $d_6$-acetone (2.0 ml) to immediately quench the reaction. $^{31}$P{$^1$H} NMR spectra were obtained from these samples at room temperature with a pulse delay of 5 s. The precursor and byproduct peaks were integrated, and from those integrals the fraction of remaining precursor was calculated. The natural log of the precursor fraction was plotted as a function of time, and from the plot the order and the half life for the precursor disappearance were determined.

**Measurement of nanocrystal size and size distribution.** TEM specimens were prepared by dipping carbon-coated copper grids into the toluene solution and allowing them to dry in air. Images taken at 500K magnification were saved in the TIF format and re-sampled using Image-Pro Express software (version 4.5). Diameter-distribution measurements of particles from the re-sampled images included 400-750 nanoparticles, taken from different spots on the grid. Using the diameter values measured at different times, and assuming spherical nanoparticle morphologies, nanoparticle volumes were calculated in nm$^3$. These values were used to construct normalized frequency diagrams or crystal-size distributions (CSDs). The volume data were binned using the minimum bin width (5 nm$^3$) that avoided excessive noise or discontinuities in the CSDs.
Similar specimens were also used for high-resolution TEM (HRTEM) studies. Nanoparticles obtained at both early and late times in a kinetic run were examined. The number of particles imaged under HRTEM was significantly less than those counted in low-resolution studies, as these HRTEM studies were primarily for examining nanoparticle crystallinity.

**Kinetics of Ag nanoparticle growth measured by UV-vis spectroscopy.** In a typical trial, bis(triphenylphosphine)silver(I) myristate (0.044 g, 0.051 mmol) and AIBN (0.05 g, 0.31 mmol) were dissolved in 4% w/w poly(1-hexadecene)$_{0.67}$ - co- (1-vinylpyrrolidone)$_{0.33}$ in 1,2- dichlorobenzene (10 ml) in a 50-ml round-bottom flask. The stirred mixture was heated at 130.0 ± 0.1 °C in a 300 ml oil bath connected to an Ace Glass temperature controller. Aliquots (0.1 ml) were taken at specific times and dispersed in 4.0 ml of cyclohexane. The diluted samples were then transferred to 1-cm path-length quartz cuvettes and UV-vis measurements taken. Baseline correction was performed before each measurement.

UV-visible data were reanalyzed using Origin software (version 7.5) by nonlinear least-squares fitting. Before fitting, the data were converted from wavelength (nm) to energy (eV) units, and then fit with a sum of three exponential functions for the background, and one Lorentzian function for the plasmon peak. The sum of the three fitted exponentials was then subtracted from the data and the resulting background-subtracted data refitted by a Lorentzian function. The height of this Lorentzian was determined as a function of time as nanoparticle growth proceeded.

Separately, a calibration curve was constructed for correlating the height of the Lorentzian-fitted plasmon peak with the mean diameter of Ag nanoparticles. Nanoparticles
were harvested from similar kinetic trials at various times and their mean diameters determined by analysis of TEM images (see above). The UV-vis spectra of these specimens were recorded, and subjected to the fitting procedure described above. Mean diameter vs. plasmon-peak (Lorentzian) height was then plotted as a calibration curve, allowing nanoparticle mean diameter in the kinetic trials to be extracted from the UV-vis data.

**Crystallographic procedures.** Crystals of [(PPh₃)₂Ag(O₂CC₁₃H₂₇)] suitable for X-ray structure determination were grown from a concentrated benzene solution at room temperature over a 24 h period. A specimen having dimensions of 0.35 × 0.22 × 0.08 mm³ was selected for analysis. A Bruker APEXII Kappa Charge Coupled Device (CCD) Detector system single-crystal X-Ray diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was used for the preliminary examination and data collection. Final data collection and data integration were performed using APEX2 and SAINT software packages (Bruker Analytical X-Ray, Madison, WI, 2007). Cell constants were determined by a global refinement of xyz centroids of 9977 reflections. Structure solution and refinement were carried out using the SHELXTL-PLUS software package. Direct methods were used to solve the crystal structure and full matrix least-squares methods used for the refinement. The hydrogen atoms were treated using appropriate riding model (AFIX m3). Of the two unique molecules in the asymmetric unit one showed disorder in the aliphatic chain of the myristate ligand. The disorder was resolved with partial-occupancy atoms for C96 through C99 (58:42%) and refined with geometrical and thermal parameter restraints. A projection view of the molecule with non-hydrogen atoms represented by 50% thermal ellipsoids, and showing the atom labeling is given in Figure 2-1. Crystallographic data and structure
parameters are listed in Table 1. The CCDC reference number for [(PPh$_3$)$_2$Ag(O$_2$CC$_{13}$H$_{27}$)] is 770942.
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Chapter 3

Nucleation Control in the Aggregative Growth of Bismuth Nanocrystals
Introduction

We show here that aggregative nucleation and growth contribute extensively to the formation of Bi nanocrystals from the precursor Bi[N(SiMe₃)₂]₃.¹⁻⁵ The characteristics of the aggregative-nucleation process determine the size and size distribution of the Bi nanocrystals at the end of the aggregative-growth regime. Added Na[N(SiMe₃)₂] is shown to function as both a nucleation-control and Ostwald-ripening agent.

We and others use Bi nanoparticles to catalyze the growth of semiconductor nanowires²⁻⁴,⁶⁻²³ by the solution-liquid-solid (SLS) mechanism.²⁴,²⁵ We reported a synthesis of such Bi catalyst nanoparticles that uses Bi[N(SiMe₃)₂]₃ as the Bi precursor and Na[N(SiMe₃)₂] as a size-control additive, and affords narrowly dispersed nanocrystals over the size range of 3-115 nm.⁵ However, the synthesis was developed empirically, and the nanocrystal-growth mechanism was not understood.

In the above procedure, the Bi-nanocrystal size distributions (CSDs) were observed to evolve in an interesting manner with time. An initial burst of small nanocrystals was followed by the emergence of distinctly larger nanocrystals interspersed among the smaller nanocrystals at early times. We have previously found such observations to be consistent with an aggregative nanoparticle growth mechanism.²⁶,²⁷ Consequently, we have undertaken the detailed study reported here to confirm the growth mechanism, and to thereby determine if the synthetic results above can be extended or generalized.

We and others have previously demonstrated that aggregative growth may be nucleation driven,²⁶⁻²⁸ and we have argued that aggregative nucleation provides a means for the purposeful manipulation of final nanoparticle mean sizes and size distributions. Nucleation typically occurs in an early time window that by necessity precedes growth.²⁹,³⁰
In aggregative nucleation, the process corresponds to the assembly of a critical-sized aggregate of small, primary nanocrystals, which may subsequently coalesce to a single-crystalline or polycrystalline nanoparticle that is viable for further aggregative growth.

Schematic diagrams of nucleation functions, which describe the time dependence of the nucleation rate $\Gamma(t)$, are given in Figure 3-1. The (2σ) width of the nucleation function $\Delta t_n$ determines the width of the final nanoparticle size distribution. To obtain a narrow size distribution, conditions that minimize $\Delta t_n$ must be identified. The area under the nucleation function is $N$, the number of nuclei formed, which is the number of growing nanoparticles. The amount of precursor used and $N$ determine the final nanoparticle mean size. Ideally, $N$ would be controlled by systematic changes in the maximum nucleation rate $\Gamma_{\text{max}}$, while maintaining a minimized $\Delta t_n$. 
Figure 3-1. Three schematic nucleation functions a-c having Gaussian profiles. The $2\sigma$ width of the nucleation function ($\Delta t_n$) provides a measure of the time window for nucleation. Because the $\Delta t_n$ for function b is smaller than that for function a, the nucleation process described by function b will produce a narrower nanoparticle size distribution. Functions b and c have identical $\Delta t_n$ values. However, function c has a greater maximum nucleation rate $\Gamma_{\text{max}}$ and thus a larger under-curve area, which is $N$, the number of nucleated nanoparticles. Thus, with an equal amount of precursor, the nucleation process described by function c will ultimately produce a smaller nanoparticle mean size.

In the Chapter 1 study of the coarsening of Au nanocrystals,$^{26}$ we demonstrated that $\Delta t_n$ and $N$ were systematically influenced by the concentration of a salt additive, tetraoctylammonium bromide. We further showed that the final Au-nanoparticle size and size distribution were strongly correlated with $\Delta t_n$ and $N$ in the manner described above. However, prior to the present results, we had not found experimental conditions that systematically influenced $\Gamma_{\text{max}}$. Thus, the aggregative growth of Bi nanocrystals provides an opportunity to further test the nucleation-control strategy described above and depicted in Figure 3-1.
Here we report the kinetics of Bi-nanoparticle growth from Bi[N(SiMe3)2]3 in the presence of varying concentrations of the additive Na[N(SiMe3)2]. We find that the additive concentration primarily influences $\Gamma_{\text{max}}$, while $\Delta t_n$ remains reasonably narrow. We show that the nanoparticle mean size correlates strongly with $\Gamma_{\text{max}}$, and the nanoparticle size distribution correlates strongly with $\Delta t_n$, as expected, prior to the onset of Ostwald ripening. The results establish that important advances in nanoparticle synthesis by aggregative nucleation and growth will be realized when $\Gamma_{\text{max}}$ and $\Delta t_n$ can be purposefully, systematically controlled. Table 3-1 lists the abbreviations used in this chapter.

**Table 3-1.** List of abbreviations and their definitions

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSD</td>
<td>Nanocrystal size distribution</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Nucleation rate (in s$^{-1}$)</td>
</tr>
<tr>
<td>$\Gamma_{\text{max}}$</td>
<td>Maximum nucleation rate (in s$^{-1}$)</td>
</tr>
<tr>
<td>$\Delta t_n$</td>
<td>Time window for nucleation (in min)</td>
</tr>
<tr>
<td>$\tau_n$</td>
<td>Time at which $\Gamma_{\text{max}}$ is achieved (in min)</td>
</tr>
<tr>
<td>$\tau_{\text{OR}}$</td>
<td>Onset time for Ostwald Ripening (in min)</td>
</tr>
<tr>
<td>$V_{\text{crit}}$</td>
<td>Volume of the critical aggregate (in nm$^3$)</td>
</tr>
<tr>
<td>$F_{\text{crit}}$</td>
<td>Fraction of the aggregates in the CSD having the critical volume</td>
</tr>
<tr>
<td>$\bar{V}(t)$</td>
<td>Nanocrystal mean volume at time $t$ (in nm$^3$)</td>
</tr>
<tr>
<td>$\bar{V}_{\text{lim}}$</td>
<td>Final mean nanocrystal volume (in nm$^3$), at the end of the active-growth regime</td>
</tr>
<tr>
<td>$k_g$</td>
<td>Growth rate (in s$^{-1}$)</td>
</tr>
<tr>
<td>$k_{\text{OR}}$</td>
<td>Ostwald Ripening rate (in s$^{-1}$)</td>
</tr>
<tr>
<td>$n$</td>
<td>Avrami exponent (unitless)</td>
</tr>
</tbody>
</table>
Results and Discussion

Early Time Monitoring of Nanoparticle Growth. Bismuth nanoparticles were generated at 180 ± 0.1 °C by an adaptation of the previously reported method, which was the thermolysis of mixtures of Bi[N(SiMe₃)₂]₃ and Na[N(SiMe₃)₂] in the presence of the polymeric nanoparticle stabilizer PHD-co-PVP. The process was monitored by TEM. The earliest images at 2 min revealed large populations of small (hereafter identified as “primary”) nanocrystals having a mean diameter of 1.9 ± 0.35 (one σ) nm (Figure 3-2a). At early times, a small population of significantly larger nanocrystals was interspersed among the primary nanocrystals (Figure 3-2a-d), producing bimodal size distributions. Such distributions are primary evidence of aggregative nucleation-and-growth mechanisms. Over time, the nanocrystals in the larger mode grew, as the population of primary nanocrystals progressively diminished. In the Figure 3-2 trial, the primary nanocrystals had disappeared by 100 min (Figure 3-2e). Subsequently, broadened size distributions were observed (Figure 3-2f), indicative of Ostwald ripening.
**Figure 3-2.** TEM images of aliquots taken at various times from a kinetics trial conducted at a Na[N(SiMe₃)₂] concentration of 0.062 M. Bimodal size distributions are evident in a-d. The broadened distribution in f is due to Ostwald ripening.

**Aggregative-Nucleation Functions.** The bimodality evident in Figure 2a-d results from the formation of critical aggregates of primary particles (aggregative nuclei), which coalesce to nanoparticles that are viable for further aggregative growth. We showed previously that the critical-aggregate size (expressed as a particle volume) is determined in favorable cases by the emergence of a peak in the early time CSDs. We also showed that the aggregative-nucleation function – the time dependence of the aggregative-nucleation rate – could be obtained from a plot of the fraction of nanoparticles having the critical size (Fₚₚ) vs. time.
In the present study, peaks in the CSDs at the critical-aggregate sizes were not well resolved, due to the large diameter range over which growth occurred (1.9-29 nm). We were unable to count sufficiently large numbers of nanoparticles to provide highly resolved CSDs over the large nanoparticle-volume ranges observed. One set of CSDs for the synthesis carried out at 0.049 M Na[N(SiMe₃)₂] is shown in Figure 3-3. Consequently, we chose a critical-diameter bin size of 3.5-4.0 nm by correspondence to those found in our previous studies. We did so with the confidence that if we used a bin smaller than the true critical-aggregate size, a nucleation function could not be successfully extracted from the data. Furthermore, if we used a bin larger than the true critical-aggregate size, the nucleation function should be only slightly broadened (in ∆tn) and delayed relative to that obtained at the true size.

Figure 3-3. CSDs for the Bi nanocrystal growth conducted at Na[N(SiMe₃)₂] molar concentration of 0.049 M at the times indicated in the inset legend. The data were binned using a bin size of 5 nm³. Peaks are not readily evident.
A set of nucleation functions like those in Figures 3-1 and 3-4 were constructed using the procedures reported in Chapters 1 and 2 and assuming a critical-diameter bin of 3.5-4.0 nm. We then redetermined the nucleation functions by assuming a critical-diameter bin of 3.0-3.5 nm. The two sets of functions were similar to one another, except that those determined at the smaller assumed critical size were shifted earlier in time, as expected, and gave less scatter in the $F_{\text{crit}}$ data with respect to the Gaussian fits. One such nucleation function is given in Figures 3-4.

**Figure 3-4.** Nucleation function and Gaussian fit for the synthesis conducted at Na[N(SiMe$_3$)$_2$] molar concentration of 0.049 M. The left and right axes correspond to the critical-aggregate fraction $F_{\text{crit}}$ and the scaled nucleation rate $\Gamma$, respectively.
As noted above, we previously found that Na[N(SiMe3)2] functioned as a size-control additive in Bi-nanoparticle growth, and we hypothesized that it influenced the nucleation process. Figure 3-4 is the $F_{\text{crit}}$ vs. $t$ curve extracted from a kinetics trial using a Na[N(SiMe3)2] concentration of 0.049 M. The curve was rescaled as the nucleation function $\Gamma(t)$ vs. $t$ (right axis in Figure 3-4) as previously described in Chapters 1 and 2 and will be recapitulated here for clarity. The total number $N$ of aggregative nuclei formed was calculated by dividing the total volume of Bi used by the final mean nanocrystal volume (Table 3-2). The height $h$ of a Gaussian curve is related to its area $A$ and width $2\sigma$ according to eq 1. For the nucleation function, the area is equal to $N$, the width to $\Delta t_n$ (the $2\sigma$ breadth of the time window for nucleation), and the height to $\Gamma_{\text{max}}$ (eq 2).

$$h = \frac{A}{2\sigma \sqrt{\frac{\pi}{2}}} \quad \text{(1)}$$

$$\Gamma_{\text{max}} = \frac{N}{\Delta t_n \sqrt{\frac{\pi}{2}}} \quad \text{(2)}$$

Figure 3-5 gives the nucleation functions determined at all the Na[N(SiMe3)2] concentrations studied. Individual nucleation functions are plotted with error bars as Figures 3-6 - 3-9. The maximum nucleation rate $\Gamma_{\text{max}}$, the time at which $\Gamma_{\text{max}}$ was reached $\tau_n$, and the $(2\sigma)$ width of the time window for nucleation $\Delta t_n$ taken from the Figure 3-5 nucleation functions are recorded in Table 3-2. The results reveal comparatively small differences in $\tau_n$ and $\Delta t_n$ at the various Na[N(SiMe3)2] concentrations, but significant variations in $\Gamma_{\text{max}}$ (Figure 3-5 and Table 3-2). The implications of these nucleation-parameter comparisons are
further discussed below. Clearly, the Na[N(SiMe$_3$)$_2$] additive did indeed influence the aggregative-nucleation process.

Figure 3-5. Nucleation functions for the syntheses conducted at various molar concentrations of Na[N(SiMe$_3$)$_2$] (0.10 mmol of Bi[N(SiMe$_3$)$_2$]$_3$ was used in each synthesis). The Na[N(SiMe$_3$)$_2$] concentration values are given in the inset legend.
Nucleation function and Gaussian fit for the synthesis conducted at Na[N(SiMe$_3$)$_2$] molar concentration of 0.063 M.

Figure 3-7. Nucleation function and Gaussian fit for the synthesis conducted at Na[N(SiMe$_3$)$_2$] molar concentration of 0.076 M.
Figure 3-8. Nucleation function and Gaussian fit for the synthesis conducted at Na[N(SiMe₃)₂] molar concentration of 0.087 M.

Figure 3-9. Nucleation function and Gaussian fit for the synthesis conducted at Na[N(SiMe₃)₂] molar concentration of 0.099 M.
Table 3-2. The aggregative nucleation, growth and Ostwald ripening parameters extracted from the kinetic data for Bi-nanoparticle growth as a function Na[N(SiMe\(_3\)]\(_2\)] molar concentration.

<table>
<thead>
<tr>
<th>Na[N(SiMe(_3)](_2)] (M) (Na:Bi mole ratio)</th>
<th>(\tau_n) (^{a}) (min)</th>
<th>(\Delta t_n) (^{b}) (min)</th>
<th>(k_g) (^{c}) ((\times 10^{-2} \text{ s}^{-1}))</th>
<th>(n^d)</th>
<th>(\tau_{GR}) (^{e}) (min)</th>
<th>(k_{GR}) (^{f}) ((\times 10^{-3} \text{ s}^{-1}))</th>
<th>(d_{final}) (nm)</th>
<th>(N) (^{g}) ((\times 10^{14}))</th>
<th>(\Gamma_{max}) (^{h}) ((\times 10^{11} \text{ s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.049 (4.90:1)</td>
<td>38.33 ± 0.89</td>
<td>26.69 ± 1.51</td>
<td>1.37 ± 0.02</td>
<td>3.04 ± 0.18</td>
<td>117.71 ± 10.21</td>
<td>2.48 ± 0.22</td>
<td>29.13 ± 0.32</td>
<td>2.60 ± 0.19</td>
<td>1.29 ± 0.08</td>
</tr>
<tr>
<td>0.063 (6.30:1)</td>
<td>41.42 ± 0.79</td>
<td>21.41 ± 1.60</td>
<td>1.51 ± 0.02</td>
<td>3.57 ± 0.28</td>
<td>78.95 ± 4.69</td>
<td>8.10 ± 0.74</td>
<td>20.86 ± 0.19</td>
<td>7.19 ± 0.85</td>
<td>4.47 ± 0.04</td>
</tr>
<tr>
<td>0.076 (7.60:1)</td>
<td>38.25 ± 1.10</td>
<td>19.71 ± 1.55</td>
<td>1.68 ± 0.06</td>
<td>3.76 ± 0.69</td>
<td>75.56 ± 7.86</td>
<td>6.28 ± 0.55</td>
<td>20.11 ± 0.09</td>
<td>9.17 ± 0.70</td>
<td>6.19 ± 0.02</td>
</tr>
<tr>
<td>0.087 (8.70:1)</td>
<td>36.07 ± 0.73</td>
<td>18.27 ± 0.97</td>
<td>1.62 ± 0.02</td>
<td>4.36 ± 0.38</td>
<td>88.32 ± 8.68</td>
<td>3.88 ± 0.38</td>
<td>23.15 ± 0.09</td>
<td>5.42 ± 0.33</td>
<td>3.95 ± 0.02</td>
</tr>
<tr>
<td>0.099 (9.99:1)</td>
<td>47.36 ± 0.85</td>
<td>28.83 ± 1.56</td>
<td>1.15 ± 0.03</td>
<td>3.89 ± 0.47</td>
<td>105.04 ± 14.65</td>
<td>3.47 ± 0.42</td>
<td>24.48 ± 0.19</td>
<td>4.30 ± 0.22</td>
<td>2.03 ± 0.02</td>
</tr>
</tbody>
</table>

\(^{a}\)Time taken for maximum nucleation rate to be achieved. \(^{b}\)Time window for nucleation. \(^{c}\)Growth rate. \(^{d}\)Avrami exponent. \(^{e}\)Onset time for Ostwald ripening. \(^{f}\)Rate parameter for Ostwald ripening. \(^{g}\)Total number of critical aggregates. \(^{h}\)Maximum nucleation rate.

**Particle-Growth Kinetics.** A representative kinetic profile for Bi-nanocrystal growth (obtained using a Na[N(SiMe\(_3\)]\(_2\)] concentration of 0.049 M) is shown in Figure 3-10. The growth is plotted as \(\bar{V}(t)/\bar{V}_{lim}\) vs. time, where \(\bar{V}(t)\) is the mean nanocrystal volume at time \(t\), and \(\bar{V}_{lim}\) is the limiting mean nanocrystal volume at the end of the active-growth period (see below). \(1/\bar{V}_{lim}\) is a scaling factor that allows kinetics fits from the different trials to be conveniently compared.
Figure 3-10. Kinetic data and the eq-1 fit for synthesis conducted with a Na\[N(SiMe_{3})_{2}\] molar concentration of 0.049 M. \(\bar{V}(t)\) is the nanocrystal mean volume at a specific time, and \(\bar{V}_{\text{lim}}\) is the final nanocrystal mean volume.

We have shown in Chapter 1 that pseudo-sigmoidal nanoparticle growth profiles may be well fit by eq 3.27 The first term in eq 3 is a conventional KJMA expression to fit the aggregative nucleation and growth regimes.26,42 The second term accounts for the late-time Ostwald ripening, during which the mean nanocrystal volume increases linearly with time.27,43-46 This second, Ostwald-ripening term contains a logistic turn-on function that activates Ostwald ripening at an onset time \(\tau_{\text{OR}}\). The \(w\) parameter in eq 1 determines the width of the Ostwald-ripening turn-on period, which was arbitrarily set at 3 min. The parameters \(k_{g}\) and \(k_{\text{OR}}\) are rate parameters describing aggregative growth and Ostwald ripening, respectively, and \(n\) is the Avrami exponent. Non-linear least-squares fitting by optimization of \(k_{g}, n, k_{\text{OR}}, \) and \(\tau_{\text{OR}}\) in eq 1 afforded the fitted curve in Figure 3-10. The initial
induction period is associated with aggregative nucleation, the steeply rising intermediate regime with aggregative growth, and the final slope with Ostwald ripening.

\[
\frac{\bar{V}(t)}{V_{\text{lim}}} = \left(1-\exp(-k_g t)^n \right) + \left[ \frac{(t-\tau_{\text{OR}})}{1+\exp(-2\tau_{\text{OR}})} \right] k_{\text{OR}} \tag{3}
\]

All sets of kinetic data collected as a function of Na[N(SiMe₃)₂] concentration are plotted in Figure 3-11, with their eq-3 fits. The individual plots with error bars are presented in Figures 3-12 to 3-15. The fitted \( k_g, n, k_{\text{OR}}, \) and \( \tau_{\text{OR}} \) values are recorded in Table 3-2. These values are analyzed further in the discussion. The curves exhibit quite similar pseudo-sigmoidal profiles, although a systematic variation in the Ostwald-ripening rate \( k_{\text{OR}} \) is clearly evident.

Figure 3-11. Kinetic data and the eq-1 fits for syntheses conducted at various molar concentrations of Na[N(SiMe₃)₂].
**Figure 3-12.** Kinetic data and the eq-1 fit for synthesis conducted at a $\text{Na}[\text{N(SiMe}_{3}\text{)}_{2}]$ molar concentration of 0.063 M.

**Figure 3-13.** Kinetic data and the eq-1 fit for synthesis conducted at a $\text{Na}[\text{N(SiMe}_{3}\text{)}_{2}]$ molar concentration of 0.076 M.
Figure 3-14. Kinetic data and the eq-1 fit for synthesis conducted with a Na[N(SiMe₃)₂] molar concentration of 0.087 M.

Figure 3-15. Kinetic data and the eq-1 fit for synthesis conducted at a Na[N(SiMe₃)₂] molar concentration of 0.099 M.
The nucleation function and nanocrystal size and size distribution. The largest influences of Na[N(SiMe₃)₂] concentration on the Bi-nanocrystal nucleation and growth kinetics are found in the maximum nucleation rate Γₘₐₓ and the Ostwald-ripening rate kₙₙ (see Table 3-2). The parameter Γₘₐₓ rises and falls with increasing Na[N(SiMe₃)₂] concentration over a range in which the minimum and maximum values vary over a range of nearly 6. The parameter kₙₙ rises and falls with increasing Na[N(SiMe₃)₂] concentration over a range in which the minimum and maximum values vary over a range of nearly 4 as depicted graphically in Figure 3-16. By contrast, the remaining kinetic parameters τₙₙ, Δtₙₙ, kₕ, and τₙₙ vary over ranges that are within factors of less than 2. Thus, the added Na[N(SiMe₃)₂] operates as both a nucleation-control and an Ostwald-ripening agent.

Figure 3-16. Plot showing the rise and fall of the Ostwald-ripening rate kₙₙ vs molar concentration of Na[N(SiMe₃)₂]. Na[N(SiMe₃)₂] has a solubilizing effect on the Bi nanoparticle and thus promotes Ostwald ripening.
We argued above (Figure 3-1) and previously demonstrated\textsuperscript{26} that the “final” nanoparticle size distribution should correlate with $\Delta t_{\text{n}}$, the time window for nucleation, and that the “final” nanoparticle mean size ($d_{\text{final}}$) should anti-correlate with $N$, the number of growing nanoparticles (and the area under the nucleation function described by $\Delta t_{\text{n}}$ and $\Gamma_{\text{max}}$). Here the “final” size and size distribution refer to those just prior to the onset of Ostwald ripening at $\tau_{\text{OR}}$. Because $\Delta t_{\text{n}}$ was observed to vary over such a small range here, $N$ is largely dependent on the variations in $\Gamma_{\text{max}}$. Consequently, we next examine the correlations between final size distribution and final mean size with $\Delta t_{\text{n}}$ and $\Gamma_{\text{max}}$, respectively, as a function of Na[N(SiMe$_3$)$_2$] concentration.

Figure 3-17 plots the relative standard deviation in the final nanocrystal size distribution and $\Delta t_{\text{n}}$ vs. Na[N(SiMe$_3$)$_2$] concentration. The two curves follow one another fairly closely, indicating that the narrower nucleation time windows produce narrower final size distributions, as expected (see Figure 3-1). These results parallel those we previously reported for the coarsening of Au nanoparticles.\textsuperscript{26}
Figure 3-17. Plots of the relative standard deviation in the final nanocrystal diameter distribution (black squares, left axis) and the time window for nucleation $\Delta t_n$ (red squares, right axis) vs molar concentrations of Na[N(SiMe$_3$)$_2$]. The relative standard deviation is the standard deviation in the diameter at the end of the active growth regime divided by the final mean nanocrystal diameter.

Figure 3-18 plots the final nanocrystal mean diameter $d_{\text{final}}$ and $\Gamma_{\text{max}}$ vs. Na[N(SiMe$_3$)$_2$] concentration. The two curves are nearly mirror images of one another, showing that, at a fixed amount of Bi, a larger $\Gamma_{\text{max}}$ and thus a larger $N$ produce a smaller final mean nanocrystal size, as expected (see Figure 1). The values of $d_{\text{final}}$ and $\Gamma_{\text{max}}$ are indeed anti-correlated. These results are also consistent with those reported for the coarsening of Au nanoparticles in Chapter 1.\textsuperscript{26}
Figure 3-18. Plots of the final nanocrystal mean diameter (black squares, left axis) and the maximum nucleation rate $\Gamma_{\text{max}}$ (red squares, right axis) vs molar concentration of Na[N(SiMe$_3$)$_2$].

The rise and then fall in $\Gamma_{\text{max}}$ with increasing Na[N(SiMe$_3$)$_2$] concentration indicates that at lower concentrations the additive functions as a nucleation promoter, and at higher concentrations as a nucleation inhibitor. In our prior study we argued that an ionic additive promoted aggregative nucleation by collapsing the electrostatic double layer around the nanoparticles that stabilized them against aggregation (Scheme 3-1).$^{47}$ This effect presumably accounts for the influence of Na[N(SiMe$_3$)$_2$] at lower concentrations. At higher concentrations the additive apparently performs a second, presently unidentified function that inhibits aggregative nucleation. A speculative possibility is that attachment of N(SiMe$_3$)$_2$ ligands to the nanocrystal surfaces increases the steric barrier to aggregation (Scheme 3-1).
Scheme 3-1. Schematic depiction of the speculative roles of Na[N(SiMe₃)₂] in the promotion and inhibition of aggregative nucleation.

At lower concentrations, Na[N(SiMe₃)₂] collapses the electric double layer about the Bi nanocrystals. The yellow region surrounding the Bi nanocrystal core represents the polymer coating, and the light-blue region represents the double-layer (the extent of the Na⁺ counterion atmosphere). The Na⁺ ions are depicted by plus signs, and the [N(SiMe₃)₂]⁻ ligands attached to the Bi surfaces by minus signs and N symbols. At low ionic strength (left) the Na⁺ counterion atmosphere is extended due to mutual Na⁺ ion repulsions. The extended Na⁺ counterion atmospheres on adjacent nanoparticles repel one another, preventing the close approach of nanoparticles, and thus inhibiting their aggregation. At higher ionic strength (center) the double layer collapses due to screening, and the counterion atmosphere about each nanoparticle shrinks dramatically, promoting the aggregation of nanoparticles. We speculate that at even higher concentrations, additional [N(SiMe₃)₂]⁻ ligands attach to the Bi-nanocrystal surfaces, increasing the steric barrier (right) and inhibiting aggregation.
Potential support for the latter speculation may be drawn from comparisons of the aggregative-nucleation kinetics for Bi nanocrystals in this study, and for Au\textsuperscript{26} and Ag\textsuperscript{27} nanoparticles from our previous studies. As shown in Table 3-3, the maximum nucleation rate is two orders of magnitude lower for Bi. The number of aggregative nuclei formed per mole of metal is one order of magnitude lower for Bi, establishing a larger comparative aggregative-nucleation barrier. The smaller nucleation rates and numbers for Bi account for the larger final mean diameters of the Bi nanoparticles (20-29 nm) compared to those of Au (5-7 nm) and Ag (7-8 nm).

Table 3-3. Table showing the maximum nucleation rate and the number of aggregative nuclei formed per mole of metal.

<table>
<thead>
<tr>
<th>Nanocrystal</th>
<th>$\Gamma_{\text{max}}$ (s\textsuperscript{-1})</th>
<th>$N$/mol (nuclei mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$2.63 \times 10^{13}$</td>
<td>$6.99 \times 10^{19}$</td>
</tr>
<tr>
<td>Ag</td>
<td>$1.21 \times 10^{13}$</td>
<td>$5.04 \times 10^{19}$</td>
</tr>
<tr>
<td>Bi</td>
<td>$6.18 \times 10^{11}$</td>
<td>$9.17 \times 10^{18}$</td>
</tr>
</tbody>
</table>

In the case of Ag, there was presumably no electrostatic component to the aggregative-nucleation barrier\textsuperscript{27}. For Au, the electrostatic barrier resulted from surface-adsorbed bromide ions, which are sterically small\textsuperscript{26}. For Bi, the putative electrostatic barrier results from surface-adsorbed [N(SiMe\textsubscript{3})\textsubscript{2}]\textsuperscript{-} ligands, which are very bulky. Consequently, one should expect a larger steric component to the aggregative-nucleation barrier for Bi, both before and after collapse of the electrostatic component (Scheme 1).

**Ostwald ripening.** As noted above, Na[N(SiMe\textsubscript{3})\textsubscript{2}] also behaves as an Ostwald-ripening agent under the conditions employed here, as evidenced by the increase and then decrease in the Ostwald-ripening rate $k_{\text{OR}}$ with increasing Na[N(SiMe\textsubscript{3})\textsubscript{2}] concentration.
Ostwald-ripening agents generally function by altering the concentrations or populations of the mobile transport species involved in the exchange of material between smaller and large particles.\textsuperscript{48-52} In the present case Na[N(SiMe\textsubscript{3})\textsubscript{2}] is presumably involved in the generation of soluble Bi complexes that participate in Bi transport.

Ostwald-ripening agents are known to influence nucleation under certain conditions, as we have observed here.\textsuperscript{48} Thus, an additive in amounts above a critical concentration can readily function as both a nucleation-control agent and an Ostwald-ripening agent. For synthetic purposes, one would ideally identify conditions under which the additive influences nucleation, in this case aggregative nucleation, but does not activate Ostwald ripening such that $k_{OR}$ remains very small.

Fortunately, under the synthetic conditions we previously reported,\textsuperscript{5} the rates of Ostwald ripening were vanishingly small. Those conditions employed higher Bi[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{3} concentrations and lower Na[N(SiMe\textsubscript{3})\textsubscript{2}]:Bi[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{3} ratios than were studied here. Thus, apart from presence of Ostwald ripening, the mechanism elucidated in this study applies to the synthetic conditions, and establishes that size control was achieved through systematic variations in $\Gamma_{\text{max}}$ achieved by varying the Na[N(SiMe\textsubscript{3})\textsubscript{2}] concentration.

**Conclusion**

We proposed above (and in Figure 3-1) that ideal nucleation control over nanocrystal formation requires a narrow time window for nucleation $\Delta t_n$ to ensure a narrow final size distribution, and an adjustable maximum nucleation rate $\Gamma_{\text{max}}$ to allow systematic variation of the final mean size. In the present work we have indeed achieved a systematic variation in $\Gamma_{\text{max}}$ while maintaining a small $\Delta t_n$ by addition of the nucleation-control agent
The final Bi-nanocrystal size distributions and mean sizes have been shown to vary in the predicted manner.

The results establish that the proposed, ideal form of nucleation control has been achieved, although only in a limited sense. We do not understand precisely how the nucleation-control agent influences $\Gamma_{\text{max}}$, nor why it has such a small effect on $\Delta t_n$. Paradoxically, in our previous study of Au-nanoparticle growth\textsuperscript{26} the nucleation-control agent (tetra-$n$-octylammonium bromide) exerted a strong influence on $\Delta t_n$, and little effect on $\Gamma_{\text{max}}$. Consequently, the next stage of this work will require that we determine the detailed mechanisms by which $\Delta t_n$ and $\Gamma_{\text{max}}$ may be separately, purposefully adjusted. Progress in that work should allow true rational control in nanoparticle synthesis to be realized.

**Experimental Section**

**General methods and materials.** Poly(1-hexadecene)$_{0.67}$-co-(1-vinylpyrrolidinone)$_{0.33}$ (PHD-co-PVP), Na[N(SiMe$_3$)$_2$] (as a 1.0 M THF solution packaged under N$_2$), toluene, and methanol were purchased from Aldrich and used as received. 1,3-diisopropylbenzene (DIPB) was purchased from Aldrich, shaken with concentrated sulphuric acid to remove thiophene, neutralized with K$_2$CO$_3$, washed with water, and distilled over Na. The precursor Bi[N(SiMe$_3$)$_2$]$_3$ was synthesized according to the literature\textsuperscript{4} and stored in the freezer in the glovebox. A solution containing 25% w/w PHD-co-PVP in diisopropylbenzene (DIPB) was prepared using dry DIPB and stored in the glovebox over molecular sieves. All kinetics trials were conducted in a dry O$_2$-free N$_2$ atmosphere using standard air-free techniques under ambient pressure. The purification of the Bi nanocrystals taken from aliquots during the kinetics trials was conducted in the ambient atmosphere, as was TEM sample preparation.
Collection of kinetic data for bismuth nanoparticle growth. Bi[N(SiMe$_3$)$_2$]$_3$, (69 mg, 0.10 mmol) was dissolved in the 25 wt. % PHD-co-PVP in DIPB (10 g) in a Schlenk tube, generating a pale yellow solution. To this solution Na[N(SiMe$_3$)$_2$] (450 mg, 0.498 mmol) was added. The mixture was then heated in an oil bath preheated to 180 ± 0.1 ºC in a 2.6 L oil bath connected to an Ace Glass temperature controller. Constant temperature was maintained and monitored with a Pt thermocouple. As the sample was heated, a light brown color developed within 5 min, which then gradually changed to a deep brown-black color within 10-20 min.

Removal of aliquots at prescribed times was performed by taking up a small volume of solution (0.3-0.5 mL) using a syringe needle and a new disposable syringe. Each aliquot was immediately redispersed into a test tube containing 0.5 mL of toluene. Methanol (4 mL) was immediately added to precipitate the nanocrystals. The methanol mixture containing the nanoparticles was then centrifuged for 2 min. After centrifuging, the methanol was removed. The toluene-methanol-centrifugation process was then repeated.

After purification, 0.5 mL toluene was added to the isolated nanocrystals and the mixture was sonicated for about 1 min. TEM grids were prepared within 1 h by the method described in the next section. In subsequent kinetics trials, all conditions were held constant except the amount of Na[N(SiMe$_3$)$_2$], which was varied as follows; 569 mg (0.631 mmol), 690 mg (0.764 mmol), 785 mg (0.869 mmol) and 903 mg (0.999 mmol). Nanoparticles purified very quickly after the aliquot was taken gave the cleanest TEM images.

Measurement of nanocrystal size and size distribution. Carbon Type-B, 300-mesh copper grids (Ted Pella) were used with the carbon support intact. The toluene solution of nanoparticles was further diluted as necessary to ensure a light coverage. One to two drops
of the solution were pipetted onto the grid in air and tapped lightly to remove the excess. The prepared sample was then evaporated to dryness, taking care to protect it from heat exposure, as this could cause agglomeration and ripening. All samples were prepared within 1 h of sample purification, and were analyzed by TEM within 24 h of grid preparation. No evidence of particle agglomeration was observed during TEM analysis. Digital TEM images were obtained from several locations on the sample grid using a JEOL 2000 FX instrument operating at 200 kV. The normal bright-field images were saved in a TIF format and resampled using Corel PHOTO-PAINT 9 (www.corel.com), increasing the resolution from 72 to 400 dpi. The particle diameter distributions were measured from multiple images using Image-Pro Express software (www.mediacy.com). A minimum of 400 particles were measured for each sample, and all particles in a given image were measured to obtain the most accurate ratio of small to large particles, as this greatly affected the average diameter obtained. The number of particles measured was particularly important for the bimodal early time distributions, as these samples required larger numbers of particles to form an accurate distribution. Periodically, 2000 or more particles were measured in order to compare the mean, standard deviation, and distribution shape to those obtained from smaller sample counts. No significant difference was detected on these occasions, indicating that the number of particles measured was sufficient to produce reliable statistics.
References


CONCLUSION TO THE DISSERTATION

Nucleation functions for *classical* nucleation and growth cannot presently be experimentally determined. We have shown for the first time that an aggregative nucleation function can be determined for the aggregative nucleation and growth process. Having determined nucleation functions, we have also shown that they can be manipulated by varying the ionic strength of the reaction medium. Manipulation has led to control over the width of the nucleation functions ($\Delta t_n$) and the maximum aggregative nucleation rates ($\Gamma_{\text{max}}$). Control over $\Delta t_n$ has been shown to directly influence final particle dispersities while control over both $\Gamma_{\text{max}}$ and $\Delta t_n$ have been shown to influence final mean particle sizes.

The ability to manipulate nucleation functions presents a great synthetic potential. This potential is not yet realized because we have not demonstrated how to systematically control both the $\Delta t_n$ and $\Gamma_{\text{max}}$ for the same synthetic system. Ideally one would want to maintain a very narrow $\Delta t_n$ and vary the $\Gamma_{\text{max}}$ in order to vary the final mean particle sizes. Further investigations are needed to have a clearer picture on how to systematically control both parameters of the nucleation function.

The results and analysis presented in this work demonstrate that the aggregative growth mechanism should be considered as a viable mechanism in nanoparticle size evolution. The use of CSDs in the nucleation and growth kinetics makes the analyses easily done. Thus investigations of aggregative mechanisms should be readily available to the synthetic community.