CLUSTER COAGULATION AND GROWTH
LIMITED BY
SURFACE INTERACTIONS WITH POLYMERS

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Abstract

The physical and chemical properties of metal nanoparticles differ significantly from those of free metal atoms as well as from the properties of bulk metals, and therefore, they may be viewed as a transition regime between the two physical states. Within this nanosize regime, there is a wide fluctuation of properties, particularly chemical reactivity, as a function of the size, geometry, and electronic state of the metal nanoparticles. In recent years, great advancements have been made in the attempts to control and manipulate the growth of metal particles to pre-specified dimensions. One of the main synthetic methods utilized in this endeavor, is the capping of the growing clusters with a variety of molecules, e.g. polymers. In this paper we attempt to model such a process and show the relationship between the concentration of the polymer present in the system and the final metal particle size obtained. The theoretical behavior, which we obtained, is compared with experimental results for the cobalt-polystyrene system.

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1. INTRODUCTION

The physical and chemical properties of metal nanoclusters differ significantly from those of individual metal atoms, as well as from the properties of bulk metal,\textsuperscript{1-5} and hence size regime of nanoclusters may be viewed as a transition regime between the two physical states. Within the cluster regime, there is a wide fluctuation of properties, particularly chemical reactivity, depending on the size, geometry, electronic state and packing of the cluster.\textsuperscript{6-13} Uniformity of size and spatial distribution of the metal nanoclusters is essential in the study of their properties, and can be achieved primarily by conducting their synthesis in the presence of stabilizers. These materials, such as surfactants or polymers, adsorb onto the surfaces of growing clusters and create a “shielding effect”, a chemical barrier which prevents the effects of van der Waals interactions between particles, thus inhibiting the particle aggregation process.\textsuperscript{14-23} Polymers are frequently used as stabilizers for metal clusters because they are transparent, permeable and non-conductive, and as such, do not interfere with and/or mask the potential optical, electrical and catalytic properties of these clusters.

Synthetic routes for the formation of nanoclusters include ultra high vacuum techniques (UHV) and “wet” chemical synthesis. The UHV processes, e.g. chemical vapor deposition, have traditionally dominated in the preparation of nanoclusters due to their inherent controllability, but the they lacks the flexibility necessary to manipulate a variety of properties within the same system. The chemical synthetic methods, e.g. reduction of metal halides and decomposition of organometallic complexes, are becoming more popular in recent years due to the ability to introduce stabilizing agents and therefore afford limitation of aggregate size.

The motivating physical system for this work is the chemical synthesis of nanoscale metal clusters, via the thermal decomposition of metal carbonyl complexes in solutions
containing either pure solvent or, in addition, polymers, which will result in a more viscous reaction environment. The main factors governing the nucleation and growth of the metal particles during the decomposition process, are the metal cluster size; i.e., the number of reactive sites available for chemical reactions and the mobility of the reactive metal clusters and their ability to diffuse through the solution and collide with each other. Clearly, as particle size grows, the mobility of the particles decreases, and a preferred average pseudo-equilibrium size distribution is reached. If the medium in which the thermal decompositions take place is more viscous than a pure solvent, then it is expected that the upper bound on particle mobility will be reached faster, and hence the final average particle size will be smaller.

The particular system studied in this work consists of cobalt carbonyl complexes thermally decomposed in the presence of polystyrene (PS). It is important to note that the solvent chosen for the decomposition reactions was toluene, which is a good solvent for polystyrene, and therefore it promoted the solvation of the polymer over a large composition range. Based on this experimental system, we have developed a mathematical model that aims at elucidating the effect of the initial concentration of the polymer present in the reaction solution on the final cobalt particle size obtained via the thermal decomposition mechanism, and correlate the model to our experimental results.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Polystyrene Solutions: Polystyrene (Aldrich Chemicals, $M_w = 120 \, 000$, powder form; 3.24 g) was dissolved in 250 mL of toluene (Fluka Chemical Corp., b.p. 110 °C, $d = 0.867$), to produce a $1.08 \cdot 10^{-4}$ M solution (or 1.5% wt.). Other polystyrene solutions had initial concentrations ranging from $3.60 \cdot 10^{-5}$ to $8.16 \cdot 10^{-3}$ M (corresponding to 0.5% wt. to 85%
wt., respectively). The toluene used in these solutions was dried by molecular sieve pellets (Matheson, Coleman, and Bell) and redistilled under an N₂ stream. The solutions were mixed in a 500 mL round-bottom flask for 24 h at room temperature. The more concentrated solutions (polystyrene concentrations above 40 % wt.) were refluxed under N₂ at 90-100 °C to ensure homogeneity. All solutions were either used immediately or stored under a nitrogen atmosphere.

2.2. Decomposition of Cobalt Carbonyl Solutions: The solution decompositions of either Co₂(CO)₈ or Co₄(CO)₁₂ in an inert atmosphere were performed in a closed system according to the classical stability diagram of cobalt carbynols as a function of temperature and p(CO).²⁴ Freshly prepared Co₄(CO)₁₂ crystals (1.287 g), synthesized by the method of Natta et al.,²⁵ were dissolved in 50 mL of toluene (Fluka Chemical Corp., d = 0.867), corresponding to a 4.51·10⁻² M solution. The solution was placed in a 100 mL three-neck round-bottomed flask flushed with carbon monoxide. The middle neck was equipped with a reflux condenser, a side neck with a rubber stopper, and the other neck with a thermometer. The rubber outlet was also used for sampling. The reflux condenser was equipped with a gas inlet-outlet glass-fitting device. The outlet part was connected to a tube whose other side was inserted securely into the vent. These special precautions had to be taken in order to flush away carbon monoxide gas formed during the decomposition reactions. Then the flask was placed in a controlled heated oil bath and the decomposition reaction carried out for approximately 48 h at 90 °C under a continuous N₂ stream. Stirring was essential throughout the reaction time. During the reaction period, samples were removed with a syringe at various time intervals, and their infrared spectra were recorded in NaCl liquid cells with toluene as a reference. The process was deemed complete (and pseudo-equilibrium reached) when the carbonyl absorption bands completely disappeared. The decomposition reactions performed in solutions containing polystyrene were identical to the
procedure described so far, but instead of using pure toluene as the solvent, various polystyrene solutions were used,\textsuperscript{26,27} depending on the desired polymer concentration. For polystyrene solutions of 40 \% wt. and above, some heating with vigorous stirring was necessary to ensure homogeneity of the solutions.

2.3. Particle Size Measurements: Particle size and size distribution were measured by transmission electron microscopy (TEM) using the JEOL JEM-1210 TEM instrument. Electron diffraction patterns from a TEM field emission gun were used to study the composition of the metallic particles. Samples were prepared by the dilution of the original solutions (after the decomposition process had taken place) to obtain a 0.1\% solution of polystyrene, which was applied dropwise to carbon-coated (100 \textmu m thick) TEM copper grids.

Infrared spectra were recorded on an IBM-IR-44 Fourier transform spectrometer using a demountable liquid cell purchased from Crystal Laboratories and equipped with a 0.5 mm spacer and new NaCl windows. The cell chamber was purged with dry nitrogen for at least 0.5 h before interferograms were collected. The resolution was 0.5 cm\(^{-1}\), and 3000 scans were taken for both the sample and the reference solutions. The empty, clean, and dry liquid cell was used as the background. Upon completion of each interferogram, the sample in the cell was removed by vacuum suction and the cell thoroughly flushed with toluene. When samples contained viscous solutions (over 40 wt \% polystyrene), the liquid cell was disassembled, the NaCl crystals and spacer were washed in toluene, and then the cell was reassembled using the same spacer. Spectral subtraction was performed using a subtraction factor of 1.00 in order to avoid possible spectral distortions.
3. RESULTS AND DISCUSSION

The general chemical synthesis of metal clusters has been designed to accommodate the manipulation of several process variables, and is best described in three stages: (a) The preparation of homogeneous solutions of organometallic complexes in a carefully selected solvent, i.e. it readily dissolves the organometallic complex and is also a good solvent for the polymer; (b) The mixing of these solutions with a polymer solution resulting in a viscous medium which contains the homogeneously dispersed organometallic complexes; (c) The thermal decomposition of the organometallic complexes to form uniform dispersions of small particle size. The decomposition of metal carbonyls in various media has been reported in the literature for the preparation of fine metallic particles. The thermolysis of transition metal carbonyls in solution under an inert atmosphere is a well-known technique for the preparation of pure metal powders. Typically, the clusters formed following such thermal decompositions are 50-250 Å in diameter, and are classified as the mid-size nano-regime (0-500 Å range). Some of the characteristic properties and advantages of these clusters prepared by the above method are: (a) The growth of the particles, and hence their final size, is determined mainly by diffusion distances and the driving forces between the growing clusters; (b) The desired oxidation state and surface cleanliness of the metal clusters are achieved by the strict control of the chemical and physical environments during synthesis, primarily through the variation of the decomposition atmosphere; (c) The particles may be polycrystalline\textsuperscript{22,23} and hence contain grain boundaries within the cluster. As a consequence, a large number of the atoms reside at the interface between these grain boundaries. (d) Another large fraction of the atoms in the cluster is on, or close to, the surface, and hence these atoms do not order themselves identically to atoms within the “bulk” material. (e) There are various possibilities for the subsequent reactions of
these clusters with a wide range of particles or molecules, and moreover they are small enough to allow for a homogeneous dispersion within a polymer matrix.

Since highly reactive intermediate species are formed during the decomposition reaction of metal carbonyls, there are two major pathways for reaction available for these species: (a) They can aggregate or fragment to form larger or smaller clusters, according to the following general mechanism, respectively:

$$\text{Co}_j^{(0)} + \text{Co}_k^{(0)} \rightarrow \text{Co}_{j+k}^{(0)},$$  

$$\text{Co}^{(0)}_j \rightarrow \text{Co}_h^{(0)} + \text{Co}_i^{(0)},$$

where $\text{Co}_j$ is a randomly chosen cobalt cluster with $j$ units (or fragments, defined as $\text{Co}_1$), $j, k = 1, 2, \ldots$, where $j + k$ is conserved, and $h + i = j$; and (b) They can interact with the polymer, according to the following mechanism:

$$\text{Co}_j^{(0)} + \text{PS} \rightarrow \text{Co} - \text{PS},$$

where $j = 1, 2, \ldots$, resulting in metal attachment processes which may, in some cases, lead to polymer degradation and/or crosslinking. Such cases, which are a result of the presence of reactive functional groups on the polymer chains that cause extensive metal-polymer interactions, are not considered in this paper. Polystyrene exhibits only a limited degree of interaction with the cobalt cluster fragments, via the weak coordination between the $\pi$-orbitals of the arene group on the polystyrene and the $d$-orbitals of the cobalt clusters. We are currently studying systems in which polymer degradation and/or crosslinking are extensive, and those results will be published in the near future. All the reactions described here are considered at 90$^\circ$C and in the presence of $N_2$. 
The overall chemistry of the system will therefore be a combination of both pathways described above, and will be determined by the type of the reactive groups of the polymer in solution and the nature of the metallic species formed.

The overall chemical reaction considered in this work is given by:

\[ n[Co_x\{CO\}_y] + PS \longrightarrow Co_m^{(0)} + Co - PS*, \]  

where * stands for a metal-polymer complex compounds, \( x = 1, 2, 4 \) or 6 and \( y = 4, 8, 12 \) or 16, respectively, \( y/x \leq 4 \) (according to the coordination chemistry of metal carbonyl complexes\(^\text{30}\)), and \( m = j + k \) in Equation 1. In the main reaction, the clusters are formed from smaller ones. The \( Co-PS^* \) complexes formed during this process are the products of the secondary reaction described in Equation 2, which competes with the main coagulation-fragmentation process described in Equation 1. The extent of the secondary reaction depends on the reactivity of the cobalt precursor and on the interaction coefficient between the reactive cobalt species and the polystyrene molecules. Therefore, the rate of the main coagulation reaction will depend not only on the concentration of the cobalt precursor and the rate coefficients of coagulation and fragmentation, but also on the concentration of the available reactive sites on the polystyrene in the system which are capable of interacting with the cobalt precursor.

In this manuscript we present a mathematical model to qualitatively understand the dynamics of the complex chemical system under consideration. The model is as simple as possible, but reflects the main chemical features of the system. To our knowledge, no attempt to model chemical systems of this kind has been reported to date.

In order to translate the physical system considered here into mathematical terms, we first scale the time variable by multiplying it by the coefficient of reaction between cobalt fragments and polystyrene, \( \lambda \), a positive constant, and the initial cluster mass \( C \), also a positive constant. \( \lambda \)
in this case is analogous to the Flory-Huggins interaction parameter, and it represents the strength of the interaction between the metal clusters and the functional groups of the polymer. Then we define $c_j$ as the concentration of Co clusters of size $j$ divided by $C$ and similarly, $p$ as the concentration of the reactive sites on the polystyrene, whose initial value is assumed to be a linear function of the polymer concentration, divided by $C$. For the model developed in this paper, we assumed that the only significant irreversible interaction between cobalt fragments and polystyrene will occur for $c_1$ with a coefficient of reaction $\lambda$, while for other clusters, $j \geq 2$, the interactions with the polystyrene will be reversible and weaker. Therefore, each $c_1$ particle, which is involved in this interaction, will be excluded from further participation in the main coagulation reaction. Moreover, the chemical bonding between the $c_1$ particles and the polystyrene reduces the number of reactive sites on the polymer and hence, limits the extent and rate of the cobalt-styrene interaction. It is important to stress that the overall chemistry of the system and the final particle size distribution of the cobalt clusters are dependent on the relative importance and contribution of the two competing reactions. These considerations, as we will see later, will be reflected in the results obtained from our model, which will illustrate the main features of the dynamics of the system, while disregarding a more exact and detailed description.

The process can therefore be modeled by the following system of nonlinear differential equations:

$$ \begin{align*}
\dot{c}_j &= \frac{1}{2} \sum_{k=1}^{j-1} [R_{j-k,k} c_{j-k} c_k - Q_{j-k,k} c_k] - \sum_{k=1}^{\infty} [R_{j,k} c_j c_k - Q_{j,k} c_{j+k}] - \delta_{1,j} c_1 p, \\
\dot{p} &= -c_1 p,
\end{align*} $$

(4)
for \( j = 1, 2, \ldots \), together with initial conditions satisfying \( \sum_{j=1}^{\infty} j c_j(0) = 1 \) and \( p(0) = p_0 \). In Equation 4, \( p_0 \) is the initial dimensional concentration of reactive sites divided by \( C \), \( R_{jk} \) is the dimensional coefficient of coagulation divided by \( \lambda \) and \( Q_{jk} \) is the dimensional coefficient of fragmentation divided by \( \lambda C \). All are non-negative and dimensionless. Since, as we pointed out before, a pseudo-equilibrium state is reached as a consequence of the fragmentation process and the decrease in the mobility of large clusters, we assume that the concentration of clusters whose size is larger than some finite \( N \) is negligible. This is also reflected in our simulation, and therefore, the \( \infty \) bound on the summation in Equation 4 can be replaced by \( N-j \). Note that in that case, the conservation of mass is assured. When the \( \infty \) bound is left in the summation, conservation of mass may be lost for \( t \geq t_c \) \(^{32}\) for some non-negative \( t_c \) (\( t_c \) = gelation time). In that case, the model will be valid up until \( t = t_c \).

As we pointed out before, and as it is reflected in the model, the process of metal coagulation and cluster formation (independent of the existence of polymer interactions) is a complex series of reactions, which can be grouped into two categories: (a) The growth of clusters either by the formation of atom-atom bonds between two metal fragments (metal fragment = \( c_j \)) and between a small cluster and a metal fragment, or by the development of surface-surface interactions between two large clusters; and (b) The decomposition of large metal clusters into smaller fragments. In order to properly model these processes, it is important to construct the appropriate reaction rate expressions both for the cluster formation step and the cluster dissociation step (with or without polymer interaction).

The simplest coagulation expressions found in the literature which are pertinent for our model are: \( R_{jk} = j^\alpha k^\alpha \) (predominantly chemical bond)\(^{34-40}\) and \( R_{jk} = j^\alpha + k^\alpha \) (predominantly surface interactions)\(^{34,35}\), where in both cases \( 0 \leq \alpha \leq 1 \). In this model, we recognize the fact that
there is a decline in particle mobility through the medium as a function of increased particle size. Moreover, the presence of the polystyrene molecules in the reaction solution contributes to the formation of a viscous medium\textsuperscript{41,42} which will impose an upper bound on the ability of larger clusters to interact via surface-surface interactions, and hence these types of interactions will have a negligible contribution to the overall coagulation process. These assumptions are consistent with the fact that in large clusters the fraction of atoms on the surface is small compared to the total number of atoms in the cluster, and therefore only this small fraction is essentially coordinatively unsaturated. In effect, we can view large clusters of being thermodynamically stable in real time. This is not the case for small clusters whose surface atoms represent a considerable fraction of the total metal mass. In this case, the model has to promote the growth of particles formed from smaller fragments, because this growth will minimize their free energy by reducing the number of coordinatively unsaturated surface atoms.\textsuperscript{43,44}

Therefore, the expression that we propose for the coefficients of coagulation of the cobalt fragments in our model (with or without polymer interactions) is:

\[ R_{j,k} = \frac{\sigma \cdot \mu}{j+k} j^\alpha k^\beta + \frac{j+k}{\sigma} \frac{1}{j^\beta k^\beta}, \]

for \( j, k = 1, 2, \ldots, \) where \( 0 \leq \alpha, \beta \leq 1, \ 0 < \mu \leq 1 \) is a weighting parameter that denotes the fraction of cobalt clusters that are permitted to enter into the coagulation reaction (\( \mu = 1 \) if no polymer is present), and \( \sigma > 0 \) denotes the critical size of the cobalt clusters beyond which the coagulation rates will drop as a function of size increase. The first part of the equation describes the mechanism of cluster formation due a combination of chemical bonding (for small clusters) and surface interactions (for larger clusters), without specifying the critical crossover cluster size.
The second part of the equation incorporates mobility and diffusion considerations into the rate expression, by reducing the contribution of the larger clusters, due to their lower mobility and slower diffusion through the reaction medium. The dissociation of cobalt clusters (i.e. fragmentation of cobalt cluster flocculates) into smaller particles has a direct impact on the final equilibrium cluster-size distribution of the system. We assume that large clusters dissociate preferentially into smaller clusters of similar size rather than into clusters with a large variation in size. Therefore, the expression that we propose to describe the dissociation of large cobalt clusters into smaller clusters is:

\[ Q_{j,k} = \frac{\eta j^\gamma k^\gamma}{j^\gamma + k^\gamma} \]  

for \( j, k = 1, 2, \ldots \), where: \( 0 \leq \gamma \leq 1 \), and \( 0 < \eta \leq 1 \) is a weighting parameter that denotes the fraction of cobalt clusters that undergo dissociation.

In order to qualitatively test our model, Equation 4 has been solved numerically using a Runge-Kutta method of order four with 0.01 as time-step and for \( N = 400, \alpha = 0.1, \beta = 0.5, \gamma = 1, \eta = 0.0001, \sigma = 200 \) and \( \mu = 0.1 \). These values of the parameters have been chosen such that the solution reflects a pseudo-equilibrium situation in which there is a preferred cluster average size or, in some cases, preferred average sizes. In Figure 1 we can see a graph of these preferred average sizes as a function of \( p_o \). The value of \( \eta = 0.0001 \) in Equation 6 shows that for a system with \( N = 400 \), the fraction of clusters which undergo fragmentation is low, and so the system is governed primarily by the coagulation processes. Also, \( \mu = 0.1 \) in Equation 5 indicates that only a fraction of the \( c_1 \) clusters is allowed to enter the coagulation reaction and the remainder will react with the polymer. However, the second term in the equation, which represents the contribution of the larger clusters whose mobility has been diminished, is not
affected by the interaction with the polymer (since according to this model, only $c_i$ clusters have an irreversible bonding with the polymer), and hence, equal weight has been given to both coagulation mechanisms. This is further supported by the fact that the crossover cluster size is a cluster containing half the number of $c_i$ fragments in the system. Other values for these parameters may be chosen for a different number of initial precursor fragments (N) and a different operating temperature. The first condition will dictate the optimal value for the crossover cluster size, the fraction of clusters undergoing fragmentation and the relative weight of the two coagulation mechanisms. The second condition, temperature, will directly influence the mobility and diffusional rates of the larger clusters and therefore will also dictate the relative weight of the two coagulation mechanisms. Moreover, the temperature will also influence the fraction of $c_i$ clusters that are allowed to react with the polymer, i.e. will be a factor in the determination of $\mu$. Due to the complexity of this system of equations (Equation 4), and the lack of extensive experimental data, we have opted to consider only the temperature of the experimental reaction.

An interesting observation that arises from our simulation results is the fact that the fragmentation of large cobalt flocculates has negligible contribution on the average particle size obtained for the system. Hence, a similar inverse dependence of average cluster size on initial polymer concentration is obtained also when Equation 4 does not contain the fragmentation term (and hence it is assumed that $Q_{jk} = 0$). However, the mobility term included in the expression for $R_{jk}$ (Equation 5), is crucial for the achievement of a preferred cluster size. In the absence of this term, the system proceeds towards gelation, independent of the presence of the polymer in the reaction medium.
Experimental results support the qualitative relationship between initial concentration of polymer in the reaction solution and the final particle average size. Cobalt carbonyl decomposition reactions were performed at 90 ºC, in toluene solutions with different polystyrene concentrations. Figure 2 shows the average particle size and particle size distribution obtained for several initial concentrations of polystyrene in solution. As the concentration of the polymer increases, a shift to lower average particle sizes and a compression of size distributions are observed. Two main effects contribute to the inverse dependence of particle size on polymer concentration: (a) As the polymer concentration increases, the solution becomes more viscous, and hence the diffusion of metallic fragments through the reaction medium to form aggregates decreases. Moreover, as fragments aggregate, their mobility decreases, and hence the impact of an increased solution viscosity is considerable; (b) As the polymer concentration increases, there are more polymer molecules capable of adsorbing onto the surface of the forming clusters (the total number of polymer reactive sites increases), thus creating a more compact “cap”. As a result, the hydrophobic interactions between the polymer molecules increase and the net effect of van der Waals attraction forces between the metal particles decreased. A transmission electron microscopy (TEM) micrograph picture of cobalt particles obtained from a decomposition reaction in the absence of PS (solvent only) is shown in Figure 3. The average particle size obtained in this case is 210.1 Å, and the particle size standard deviation is 56.26 Å. Another TEM micrograph picture of cobalt particles obtained from a decomposition reaction in a PS matrix (85% wt. PS in solution) is shown in Figure 4. The average particle size obtained in this case is 13.8 Å. Clearly, the presence of PS in the reaction medium at these extreme concentrations has a drastic effect on final average particle size, which decreases by more than an order of magnitude when the medium consists mainly of PS.
Figure 5 summarizes the experimental data obtained for media containing a variety of concentrations of PS. Not only does the average final particle size decrease with increasing initial concentration of PS, but the average cobalt size distribution decreases as well. This indicates that the presence of the polymer in the reaction medium prevents the formation of larger clusters thus inhibiting the coagulation process.

4. SUMMARY

The work presented in this paper is the first attempt to combine theoretical studies with experimental data in conjunction with the nucleation and growth mechanism of metal nanoparticles in the presence of a “reactive wall”. Since the reactive adsorption of organic molecules, amphiphiles, and in particular polymers, onto metal clusters, is the method of choice for the in situ control of particle size, it is imperative to understand the fundamental mechanisms of the competing processes that occur in such systems. Unfortunately, not many experimental data are available in the recent literature regarding the kinetics, mechanisms and thermodynamics of the formation of polymer-capped metal clusters, and there are practically no theoretical studies in this area, except those dealing with high-vacuum nucleation and growth of metal clusters in the absence of polymers. This work shows that “common sense” experimental phenomena, i.e. the inverse dependence of cluster size on polymer concentration, can be modeled qualitatively, and provide the basis for further, more quantitative analysis.
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5. REFERENCES


Figure Captions

**Figure 1:** The theoretical dependence of cobalt cluster size on the initial concentration of reactive sites of polystyrene in the reaction solution, \( p_0 \). Note that the number of reactive sites is directly proportional to the polymer concentration for a particular polymer molecular weight. The cluster size is expressed as the average number of precursor fragments, \( k_{avg} \). Each data point in the plot is the result of a full simulation cycle.

**Figure 2:** Cobalt particle size distribution as a result of thermal decompositions of cobalt carbonyl complexes in solutions containing polystyrene with different initial polymer concentrations, \( p_0 \). The cluster size is expressed as the average number of precursor fragments, \( k_{avg} \).

**Figure 3:** The TEM micrograph of zero-valent cobalt particles obtained by the thermal decomposition of cobalt carbonyl complexes at 90°C under an inert atmosphere in a toluene solution (\( D_{avg} = 210.1 \) Å). The dark regions represent the cobalt clusters.

**Figure 4:** The TEM micrograph of zero-valent cobalt particles obtained by the thermal decomposition of cobalt carbonyl complexes at 90°C under an inert atmosphere in a polystyrene matrix (\( D_{avg} = 22.9 \) Å).

**Figure 5:** The experimental relationship between average cobalt cluster size and the initial concentration of polystyrene in the reaction solution. The 85 % wt. PS concentration is considered a polystyrene matrix, and is designated as “solid state”.