SELECTIVE INTERFACIAL INTERACTION BETWEEN DIBLOCK COPOLYMERS AND COBALT NANOPARTICLES

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SELECTIVE INTERFACIAL INTERACTION BETWEEN DIBLOCK COPOLYMERS AND COBALT NANOPARTICLES

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To my parents Trevor and Debra David, and my brothers Osei, Omaree and Kareem. Without their love and support, all of my success would not be possible.
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SUMMARY

In order to optimize the synthesis of metal nanoparticle-polymer systems, there are certain processes which must be understood. Perhaps the most important one, which is the focus of this work, is the selective interfacial interaction between the block copolymer and the growing metal nanoparticles. To investigate this interaction, four different approaches were taken. The first approach looked at the strength of interaction between the competing blocks of the copolymer and the metal nanoparticles surface. This was done by looking at the competitive adsorption between the homopolymers which make the chosen copolymer and the metal nanocluster surface. The second approach looked at the effect of polymer architecture on the metal nanoclusters. Here the influence of block length and copolymer composition on the morphology of the metal nanoparticles was investigated. The third approach looked at the polymer composition and solvent effects on the phase behavior of the metal nanocluster-block copolymer nanocomposite. Finally, the influence of the metal precursor on the rate of the decomposition was examined.

The synthetic method used in this work involved the thermal decomposition of the metal precursor within different polymeric suspensions to produce the nanocomposite. It was found that adsorbed layers of PS on the cobalt nanoparticles are completely displaced by PMMA when the solvent is a common good solvent. An adsorbed layer of only PMMA is also obtained through competitive adsorption from a common good solvent. However, in a selective solvent that is poor for PS, sequential adsorption leads to the formation of mixed layers. It was shown that in homopolymer solutions, the cluster
size reaches a minimum at a finite chain MW. In the case of diblock copolymers, the only parameter (for a fixed copolymer concentration) controlling the cluster size in suspensions of di-block copolymers is the molecular weight of one block, in this case PMMA, and is indifferent to other parameters including the molecular weight of the other block (PS) or the solvent quality. It was also found that the spatial distribution of the metal clusters synthesized in-situ coincided with the morphology dictated by thermodynamically-driven microdomain structure of the block copolymer. Moreover, the overall final morphology of the nanocomposite is “locked” into place while in solution, and fast solvent evaporation does not cause this morphology to change. Finally, results showed that the rate of nanocomposite synthesis occurred faster in the PS suspensions compared to PMMA, indicating that chemical bonds between PMMA and the cobalt nanoclusters slowed the thermal decomposition of the metal precursor. So the PMMA chains provided sites for nucleation, but did not necessarily aid particle growth.
The study of periodic materials for novel use in applications such as photonic and electronic devices is an area that has continued to garner much interest. More specifically, materials which can combine certain properties such as being both magnetic and transparent are being greatly pursued. In order to possibly satisfy these needs, researchers have looked to composite materials which are based on nano-particulate metals. These materials would be able to satisfy some of the current and future technological needs because they would contain the kind of novel properties mentioned earlier. By themselves, nano-sized metals are highly unstable, and can aggregate or be oxidized in air. In order to solve this issue, the sequestering of these particles into a dielectric matrix can lead to easier ways of handling and stabilization. One such matrix material is polymers, because of the range of physical and chemical properties that they possess. Polymers can be insulating or conducting, they can possess a hydrophobic or hydrophilic nature, and they can also exist in a glassy or rubbery state. This variety of properties makes the use of polymers very appealing. Perhaps more importantly, polymers are an excellent candidate to act as stabilizers for metal nanoparticles. Therefore these polymer imbedded nanostructures or nanocomposites, which would contain a certain degree of tenability, should find many applications in the devices or technologies of the future. In order to create nanocomposite materials that are useful, there should exist a certain level of periodicity and ordering. This is most important in the optical applications of these materials. One existing analogy to this type of material are photonic crystals. Photonic crystals can be thought of as a periodic structure whose lattice constants are comparable to that of the wavelength of light. This arrangement creates a structure in which there are alternating low and high dielectric regions, and the formation of photonic band gaps. These photonic crystals are generally formed by colloidal spheres, which self assemble into crystalline arrays. Research is being done to fabricate colloidal
particles with specific properties such as size and surface properties. Photonic crystals can either be one, two or three-dimensional.

Figure 1.1 Example of 1D, 2D and 3D photonic crystal

Figure 1.1 is a schematic of a photonic crystal design. 2D arrays have found uses in optical microlenses, while 3D structures have been considered for several applications including optical transistors and waveguides.

In order to create these types of periodic structures using polymers, the self-assembling nature of block copolymers has been found to be a useful technique in the creation of templates for nanocomposite synthesis. Block copolymers can be thought of as two or more homopolymer chains joined together covalently at one end to form the more complex block copolymer macromolecule \(^3\), as seen in Figure 1.2.
Due to the immiscibility of the constituent blocks, the blocks would tend to separate in order to lower the enthalpy of mixing, which is generally positive for polymer blends. But since the blocks are covalently bonded on one end, their ability to phase separate is restricted, and this gives rise to a variety of unique microstructures. In fact, phase separation creates several types of periodic self-assembled morphologies as illustrated in Figure 1.3. The particular morphology is a function of the composition, interaction and molecular weights of the constituent blocks.\textsuperscript{4} The resulting periodic structures have many applications in the field of nanotechnology, including electro-optical applications.\textsuperscript{5}
The inherent dielectric difference between blocks in most block copolymers is normally small.\textsuperscript{19} Hence their use in photonic applications, which require larger differences in dielectric contrast, is limited. One way to address this challenge is by the incorporation of nanoparticles into specific microdomains of the block copolymer. These nanoparticles, which can be selectively incorporated into a specific block of the copolymer,\textsuperscript{6,7} (Figure 1.4) will cause a substantial increase in the dielectric constant of that particular microdomain. This will allow the refractive index to be manipulated with a certain degree of control, and create nanocomposites that can be used in optical applications.\textsuperscript{8,9,10}

In order to produce useful composites, the size and shape of the nanoparticles must be controlled, just like in photonic crystals, since these properties can affect the optical properties of the composite.\textsuperscript{11} The size and shape of the nanoparticles may be controlled by the use of block copolymers which act as stabilizers for the growing nanoparticles.\textsuperscript{12,13,14,15,16} Polymers are useful as stabilizers because while they restrict the size regime of the metal nanoparticles, they are transparent and nonconductive, and so do not interfere with the possible optical properties of the metal clusters.\textsuperscript{16} Because of their size, nanoparticles are also useful since they will not cause scattering and loss of the light wave signal.

![Figure 1.4 Illustration of self-assembly of block copolymers, with metal nanoparticles incorporated.](image)

There are a variety of methods that have been used to synthesize metallic nanoparticles within a diblock copolymer matrix. One method includes the adsorption of the metal atoms onto the more reactive sites of the polymer, when that polymer is exposed to metal vapors.\textsuperscript{17} A second technique includes the introduction of a metal salt into a polymer solution, followed by the reduction of the salt to leave metallic clusters.\textsuperscript{18}
In this approach, the organometallic precursor is mixed with the polymer, followed by nucleation and growth of the metallic particles. A third technique involves casting a film of the copolymer/metal precursor mixture, followed by heating.\textsuperscript{12} Block co-polymers may also provide a more attractive method to the synthesis of periodic electro-optical materials, since with organic materials, the properties can be changed or tailored at the molecular level. This work focuses on studying the selective interaction between the different blocks of the chose copolymer, PS-b-PMMA and cobalt nanoparticles.
CHAPTER 2

BACKGROUND

2.1 Nanocomposite Historical Overview

The discovery of inorganic nanoparticles can be traced back to the early days of documented chemistry experimentation. In 1570, for example, Paracelsus reported the synthesis of gold nanoparticles dispersed in liquids. This was called aurum potabile or potable gold. In 1677, the synthesis of potable silver was first recorded. Colloidal metals have also been used for their optical properties dating back to the mid 16th century. Inclusion of metal nanoparticles in glass allowed them to create colored materials that absorbed light without much scattering. The synthesis of purple, violet and almost black nanosized gold particles for use in paints, was described as early as 1765. And in 1802, the relationship between the different colors obtained with gold colloids and the size of the actual particle was established.

The preparation and study of metal-polymer nanocomposite materials has been documented since the early mid 1800’s. One of the oldest known attempts for the synthesis of metal-polymer nanocomposites that has been found in the literature dates back to 1835. In this reference, a gold salt was reduced in the gum arabic, and a nanocomposite material was obtained by coprecipitation with ethanol. Around 1900, there were reports of the production of polymer based nanocomposites made with uniaxially oriented inorganic particles. Dichroic plants and fibrils (like linen, cotton) were prepared by adding solutions of silver or gold salts and then reducing the corresponding metal ions under light.
In 1904, Zsigmondy, who was later awarded the Nobel prize in Chemistry, reported that composites made of gold nanoparticles in gelatin would reversibly change color from blue to gold in the presence of moisture. He postulated that this phenomenon was due to the change in interparticle distance and the subsequent change in absorption as the material swelled. In 1910, Kolbe showed that the nanocomposite material containing gold nanoparticles had the metal in its zero valent state. In the decades that followed, composites based on other metals (such as Pd, Pt, Cu, Hg) were produced and studied. The optical effects noticed in these nanocomposite films were found to be dependent on the element used, and the first set of optical spectra based on nanocomposite films were presented in 1946.

2.2 Polymer Adsorption

In the synthesis of polymer based nanocomposite materials, perhaps one of the most important considerations is the interaction between the polymeric matrix and the surface of the filler particles. In order to produce these nanocomposite materials, one must start by examining the phenomenon of polymer adsorption. Polymers form what are referred to as adsorption layers at the interface with solid surfaces. The properties of these layers vary from those of the bulk polymer, and it is the formation of these layers that play an important role in the polymer actually adhering to the particle surface.

It should be noted that adsorption of polymers should be regarded as different from the adsorption of low molecular mass substances. The difference can be attributed to many different parameters including the macromolecular size of the polymer chains in solution, the amount of interpenetration of the polymer coils and sometimes the different shapes or conformations that a polymer can take.
Figure 2.1 Examples of different polymer conformations on a surface a) chain lying flat on surface, b) chain adsorbed with trains and loops, c) adsorbed chain with free end.

The type and thermodynamic quality of the solvent also plays a major role in polymer adsorption. It has been found for instance, that adsorption from a “poor” solvent is higher as compared to that from a “good” solvent. And generally, polymers with a higher molecular mass are found to adsorb better than polymers with lower molecular masses. The thermodynamic interaction between the polymer and the solvent that it is in, determines the conformation of the polymer chain in solution and therefore has a direct influence on the polymer-surface interaction.

Adsorption from solutions of polymer mixtures is also an area of great interest because systems may also be composed of two or more competing polymeric species. While adsorption from individual polymer solutions has garnered wide interest, a lot of work still needs to be done on adsorption from mixed polymer solutions, especially in size regimes far removed from that of a bulk surface. Initial results have shown that in a mixture of polymers, the more polar polymer adsorbs preferentially to the surface. It was also found that the quality of solvent plays a role in adsorption from mixtures. For a polyvinyl-acetate system, it was seen that weakly adsorbing PVA could be displaced by
PS molecules if they are adsorbed from a good solvent, and that PVA prevents the formation of an adsorption layer of PS if adsorbed from a poor solvent.\textsuperscript{22}

### 2.3 Block copolymers and their behavior

Block copolymers can be grouped into the same class of materials like amphiphilic molecules and liquid crystals. This class of materials called soft materials is defined by a fluidlike disorder at the molecular level and a pronounced degree of order as the length scale increases. As mentioned before, block copolymers are formed by two chemically distinct polymer blocks bonded by a covalent bond in the middle of them.

![Example of diblock copolymer PS-b-PMMA](image)

**Figure 2.2** Example of diblock copolymer PS-b-PMMA

Block copolymers can be synthesized in a number of ways using available chemical techniques. These structures can be classified based on two primary characteristics. The first one is the number of chemically distinct blocks that make up the
copolymers. The second characteristic is the sequencing of the blocks; either linear or branched.\textsuperscript{23}

**Figure 2.3** Illustration of AB copolymer configuration. a) Linear configuration b) Branched configuration\textsuperscript{23}

Because of the variety of ways that the different monomer types can be bonded, there are multiple molecular architectures available to researchers. The simplest is the linear AB diblock copolymer, in which there is a chain or block of type A monomers covalently bonded to a chain of type B monomers. When three or more different monomer types are used, the resulting copolymer is referred to as ABC copolymer. There also exists the possibility of creating the star-ABC configuration in which all of the blocks are covalently bonded in the center.\textsuperscript{23} Thus there exists a wide variety of choices available to researchers where copolymers are concerned.

The possible technological applications of block copolymers is dependent mainly on these materials’ ability to self assemble into periodic morphologies. Moreover, block
copolymers self-assemble on the nanoscale, and thus offer intriguing possibilities as templates for certain functional materials.

### 2.3.1 Block copolymer self assembly

The microphase separation which occurs in block copolymers upon self assembly is due mainly to the chemical incompatibilities between the different blocks that form the copolymer molecules. As compared to binary mixtures of low molecular weight fluids, the entropy of mixing per unit volume of different polymers is small and varies inversely with molecular weight. This means that the smallest variation in chemistry or structure between blocks A and B are enough to cause excess free energy contributions that do not favor mixing. Hence, it is the natural behavior of polymer mixtures to tend towards separation.

The non ideal part of the mixing free energy is normally given in terms of the Flory Huggins interaction parameter:

\[
\chi_{AB} = \left( \frac{Z}{k_B T} \right) \left[ \epsilon_{AB} - \frac{1}{2} \left( \epsilon_{AA} + \epsilon_{AB} \right) \right]
\]

where \(Z\) is the number of nearest neighbor monomers to a copolymer configuration cell, and \(\epsilon_{AB}\) is the interaction energy per monomer between A and B monomers. So overall, \(\chi_{AB}\) describes the free energy cost per monomer of contacts between A and B monomers. A positive value of \(\chi_{AB}\) signifies that there is repulsion between blocks A and B, whereas a negative value indicate that there is a free energy towards mixing of the two species. \(\chi_{AB}\) is normally small and positive in the case of dissimilar polymer blocks where there are no other strong interactions such as hydrogen bonding or charges.

If the covalent bond did not exist between the different blocks of the copolymer, then thermodynamics would dictate macrophase separation. Macrophase separation is the
case in which the separate phases coexist. In block copolymers, the thermodynamic forces that lead to separation are countered by the covalent bonds between the blocks. In order to keep the different blocks of a copolymer separated, copolymers chains must assume an extended configuration. Since there exists fewer possible configurations for extended polymer chains as compared to the original random coiled state, an entropic restoring force arises that serves to keep the phase separation between blocks A and B to the mesoscopic scale.

For small copolymer with fairly compatible blocks, $X_{AB}N < 10.5$ (where N is the number of total monomers). In this case, only a disordered state is predicted and no microphase separation is occurs. When $X_{AB}N > 10.5$, five ordered states are predicted to be thermodynamically stable.

![Image of self-assembled block copolymer morphologies](image)

**Figure 2.4.** Examples of self-assembled block copolymer morphologies

The first of these is the lamellar (L) phase that is stable for almost symmetric blocks. For copolymers with intermediate compositional asymmetry, a hexagonally packed cylindrical (C) phase is stable. The smaller blocks pack into the cylinders and the longer blocks exist on the convex side of the interface between the two blocks. With an increase in compositional asymmetry, the cylinders become a body centered cubic spherical (S) phase. There is a fourth phase made up of closed packed spheres (CPS) that
can exist between the disordered phase and the S phase. The final phase is predicted to be
a gyroid (G) phase that lies close to the order-disorder transition (ODT) and between the
L and C phases.

Block copolymers also have specific behavior in solution. In a neutral solvent, i.e.
a solvent that dissolves both blocks, the polymer chains are oriented randomly in
solution. When a block copolymer is placed in a solvent that preferentially dissolves one
block, micelles are formed in solution. These micelles are spherical structures in which
the inner core, or insoluble block, is shielded from the solvent by an outer shell formed
by the soluble block. This means for example, that even if the expected morphology of
the self-assembled copolymer is lamellar upon removal of the solvent, once this
copolymer is placed in a preferential solvent, micelles will develop in solution before any
actual self-assembly has taken place. So when the solvent is removed, the expected
thermodynamic morphology may not materialize.

\[ \text{Figure 2.5. Dissolution of a block copolymer in a) neutral solvent, b) selective solvent} \]

This behavior of block copolymers is one that can be used in the synthesis of
functional materials based on the combination of block copolymers and inorganic
nanoparticles. The micelles can function as a nanoreactor in which the nanoparticles can
be produced and sequestered within the polymer matrix. Depending on the application,
the nanoparticles can be produced inside the core of the micelle or within the corona. By
varying the metal precursor, conditions, and the solvent type, which determines the
chemical composition of the core and corona, one can influence the location of the metal nanoparticles.

2.3.2 Block copolymer micellization

Researchers have already used the core of micelles to synthesize metal nanoparticles of specific sizes. The process usually involves the impregnation of the micellar core by the metal salt before the salt is reduced to its metallic state. This impregnation usually occurs through the formation of complexes or ion-pairs between the metal precursor and the species in the core of the micelles. Through this process, the location and/or size of the nanoparticles can be controlled because of the confinement by the micelles themselves. For particles embedded within the core of the micelles, there are two main configurations which have been observed (fig 2.6). The first is the “cherry” morphology in which only one metal colloid is present in the core. The second configuration is the “raspberry” morphology in which several small colloids are located inside the micelle core.25
Figure 2.6 Illustration of the preparation of metal nanoparticles within the micelle core of an amphiphilic diblock copolymer and the resulting morphologies.

Similar to the core embedded morphologies, there are also two main configurations observed when the particles are situated with the corona of the copolymer micelles (fig 2.7). The first one is referred to as the “strawberry” morphology and is formed when the metal nanoparticles are located fairly close to the micelle core, due to appreciable hydrophobic interactions between the metal particles and the hydrophobic micelle core. In this case, the particles are arranged in a spherical pattern around the core. The second configuration is the called the “red currant” morphology and is formed when the particles are distributed throughout the corona without any tendency to associate with the micelle core.25
2.4 Nanocluster nucleation and growth

For this work, cobalt carbonyl will be the metal precursor used to produce zero valent cobalt nanoparticles within the polymer matrix. Cobalt carbonyl was chosen because of its well known chemistry and characterization. When these carbonyls are heated, CO is released leaving the cobalt atoms to aggregate into the nanoclusters. There are certain advantages to this preparation technique including a) the particle size is determined mainly by the diffusion distance and driving forces between the clusters, b) the chemical and physical control during synthesis allows for obtaining the desired oxidation state, c) the particles may be polycrystalline and have grain boundaries which
means that a large number of atoms reside at the interface between the grain boundaries, d) a large fraction of the nanocluster’s atoms reside at the surface and thus they do not order themselves similarly to the bulk and finally there are many possibilities to react these fragments in situ with a wide variety of molecules.26

Previous researchers have shown that the decomposition of cobalt carbonyls proceeds in two distinct steps:

\[
\begin{align*}
2\text{Co}_2(\text{CO})_8 & \rightleftharpoons \text{Co}_4(\text{CO})_{12} + 4\text{CO} \downarrow \quad (1) \\
\frac{k}{4} \text{Co}_4(\text{CO})_{12} & \rightarrow \text{Co}_k + 3k \text{ CO} \downarrow \quad (2)
\end{align*}
\]

In the first reaction, the \( \text{Co}_2(\text{CO})_8 \) first decomposes into the intermediate \( \text{Co}_4(\text{CO})_{12} \). This then subsequently decomposes into metallic Co. Previous work has shown that the first step proceeds by the removal of a CO group from the coordination sphere of \( \text{Co}_2(\text{CO})_8 \) to generate \( \text{Co}_2(\text{CO})_7 \). This latter species then reacts with \( \text{Co}_2(\text{CO})_8 \) to form \( \text{Co}_4(\text{CO})_{12} \) and the release of three more CO.26 This reaction is governed by the movement of the molecules through the viscous medium and their ability to combine with each in solution.

In the second step, the stripping of CO groups from the coordination sphere of \( \text{Co}_4(\text{CO})_{12} \) leads to a cascade of electron-deficient cobalt fragments which react to form cobalt complexes. As the Co/CO ratio increases, the solubility of the clusters decrease, and this leads to the actual colloidal reaction. The growth of the particles during this final step can be described by the following series of nucleation and growth reactions:
Cluster stepwise growth:

Co\textsubscript{j} + Co\textsubscript{l} \rightarrow Co\textsubscript{j+l} \quad (3)

Cluster aggregation:

Co\textsubscript{j} + Co\textsubscript{k} \rightarrow Co\textsubscript{j+k} \quad (4)

Cluster dissociation:

Co\textsubscript{k} \rightarrow Co\textsubscript{i} + Co\textsubscript{j} \quad (5)

In this study, the nanoparticles will be stabilized using either homopolymers such as polystyrene (PS) and polymethylmethacrylate (PMMA), or the diblock copolymer PS-b-PMMA.

\[\text{\includegraphics[width=0.2\textwidth]{polymers.png}}\]

**Figure 2.8** Illustration of polymers used in this study.

### 2.5 Nanocluster Properties

Metals develop many new properties in going from the bulk to nanoscale, and in composites with polymers novel functional materials can be produced. Many of the new properties seen in nano-sized metals can be attributed to the quantum size effects.\(^2\) These are the electron confinement and surface effects. The effects depend on the actual size of the nanoclusters, and thus can be tuned to meet desired requirements. The confinement
effects are produced because in nano-sized metal domains, the electrons are allowed to move in a very limited space. This means that their states are quantized similar to that of atoms. The surface effects arise because as the size decreases, the properties are influenced more by the surface atoms and less by the inner atoms of the material. Also the surface nature of the nanoparticle varies when compared to the bulk. Atoms on the surface of the bulk material generally lie in the basal planes of that crystalline structures, but they become mainly edge and corner atoms when there is a decrease in size down to the nano-regime. Because of the small coordination number of edge and corner atoms, they are very chemically reactive, catalytically active and highly polarizable compared to the atoms in the bulk state. Thus there are interesting applications that can be envisioned using nano-sized metal particles.

One major property which changes with a decrease in particle size is the electronic properties of these materials. For nanoparticles, the electronic energy levels are not continuous like the bulk state, but are discrete as a result of electron confinement. Thus properties like electrical conductivity and magnetic susceptibility show quantum size effects. The discrete nature of energy levels in nanoparticles also changes the characteristic spectral features of the nanoparticles. In the visible range, the electronic absorption spectra of metal nanoparticles are controlled by plasmon bands. It is these surface plasmon excitation which give rise to the different colors of metal nanoparticle solutions. This also depends on the dielectric constant of the surrounding medium and the diameter of the nanoparticle itself. As was mentioned earlier, magnetic properties also change based on the size on the particle. It has been shown that as the dimensions tend to the nanoregime, the coercivity of the particles tend to zero. Thus nanoparticles can be superparamagnets without the associated coercivity or retentivity. It has also been seen
that as the particle size decreases, the magnetic moment per atom increases. Therefore nanoparticles can also find new applications in which the magnetic effect is important.

The chemical properties of metals also change based on the decrease in size to the nanoregime. The surface area of nanoparticles increases drastically with a decrease in size. For example, a metal nanocluster that is 1nm in size will have 100% of its atoms on the surface. It is therefore expected that as the surface area increases, these nanoparticles will show increased levels of reactivity. Also, the change in electronic structure due to quantum confinement will give these particles new catalytic properties.

For example, a study done at low temperature has shown that during the interaction between O₂ and Ag nanoparticles, dioxygen was dissociated into the atomic oxygen species. Whereas on bulk Ag, the adsorbed oxygen species at 80K is O²⁻. Work has also been done on other metals such as Cu, Pd, Pt and Ni which show a striking relationship between catalytic ability and particle size. One illustration of this is the interaction between carbon monoxide and Cu. Carbon monoxide would desorb from a bulk Cu surface above a temperature of 250K. However, smaller Cu particles can retain CO up to higher temperatures. This same observation has been noted in work done with Pd particles.²

2.6 Methods for producing nanocomposites

As was mentioned before, polymer nanocomposite materials offer many new possibilities because of the novel properties that these materials may possess. The amount of research into the synthesis of polymer based nanocomposites has increased over the last few years, and there has also been a subsequent increase in the techniques used to produce them. The techniques for producing metal-polymer nanocomposites fall into two
general areas. They can be designated as *in situ* or *ex situ*. During the *in situ* synthesis, the metal precursor is normally introduced to the polymer in solution form followed by reduction of the metal ions using chemical means, heat or UV radiation. During *ex situ* synthesis, the metal nanoparticles are first synthesized and stabilized, and then subsequently dispersed in the polymeric medium. The following discussion will highlight some of these synthesis techniques.

Morkved et al first prepared thin films of block copolymers on NaCl crystals by spin coating. Two different films were prepared. The first film was the lamellar phase of a polystyrene-b-polymethylmethacrylate (PS-b-PMMA) copolymer using a symmetric copolymer. The second film used an asymmetric polystyrene-b-poly(2-vinylpyridine) copolymer that resulted in thin films of the spherical phase. After the films were prepared, gold metal was resistively evaporated onto the polymer films at room temperature and at a pressure of 5 x 10^-6 torr. The samples were annealed for at least 24 h under vacuum and 145°C, and then left to cool to room temperature. The NaCl substrate was then dissolved leaving a free standing film that was characterized using TEM. The TEM micrographs showed that the gold nanoparticles oriented themselves in the same way as the underlying polymer domains. This means that the gold particles on the lamellar film oriented themselves into wormlike stripes matching the lamellae of the copolymer, while on the asymmetric film, the particles appeared to mirror the packing of the PVP spheres in a PS matrix (fig 2.9).
Figure 2.9 TEM micrographs of structures obtained when copolymer films were exposed to gold vapor

Figure 2.10 shows the resulting TEM micrograph from a different technique employed by Cohen and his group for the incorporation of metal nanoparticles into a block copolymer matrix. Firstly, a polymer solution that contained Co$_2$(CO)$_8$ as a precursor was made into a film by allowing the solvent to evaporate. The film was then allowed to dry under vacuum overnight and pieces of the film were cut and heated to decompose the metal precursor into Co particles. The particles were found to have nucleated in the more reactive polymer domain of the copolymer which was the P2VP block in this case and also corresponding to a lamellar morphology.
Figure 2.10 Lamellar morphology of solution-cast PS_{91,300}-b-P2VP_{115,000} with Co nanoparticles seen in the P2VP domains.

Thomas et al. used a technique in which the metal clusters had been pre-formed using standard reduction methods for the stabilization of metal colloid particles. These particles were then placed into a block copolymer solution and aggregated into a specific block within the copolymer based on the interaction between the molecules used to stabilize the nanoparticles and the functional groups on the copolymer.

Figure 2.11. One-dimensional self-assembled dielectric lattice made of SI2VP triblock with TOPO coated CdSe nanocrystals sequestered in the 2VP phase.
In this case the researchers used stabilized CdSe nanoparticles dispersed in a triblock copolymer solution of poly(styrene/isoprene/2VP). Because of the surfactant molecule used to stabilize the nanoparticles, the particles were sequestered into the 2 vinyl-pyridine domains as shown in Figure 2.11.

Moller and his group used the self assembly of diblock copolymers into micelles which acted as compartments for the formation of the nanoparticles. In this case they dissolved copolymers of PS-b-P2VP in toluene. The PS is soluble in toluene while the P2VP block is insoluble in this solvent. This caused micelles of the block copolymer to form with the P2VP block in the core of the micelle. Solid HAuCl₄ was then added to this solution and AuCl₄⁻ counterions were bound in the polar core of the micelles.

![Image](image1.png)

**Figure 2.12** Transmission electron micrographs of thin films cast from micellar solutions of PS(190)-b P[2VP(HAuCl4)0.5(190)]. (a) Micelles before treatment with anhydrous hydrazine. (b) Gold particles with a diameter of 9 nm in each block copolymer micelle after treating with anhydrous hydrazine.
Figure 2.12a) shows a TEM micrograph of the micelles loaded with AuCl$_4^-$ ions before reduction. The solution of HAuCl$_4^-$ loaded micelles was mixed with a solution of anhydrous hydrazine which reduced the Au$^{3+}$ ions to zero valent gold particles. Figure 2.12b) shows the micelles with the gold particles after reduction took place. The size of these particles were controlled by the original amount of HAuCl$_4^-$ loaded into the micelles.

This method produced the desired nanoparticles in the core of the micelle. There are also methods available to produce the nanoparticles in the corona of the micelle. One such technique was used by Zhao et al.$^{27}$ In this method CdS nanoparticles were stabilized in the corona of a PS-b-P2VP copolymer. One of the methods involved using the transition from core embedded to corona embedded nanoparticles. They started with compound micelles made up of single micelles bridged by free 2VP segments, in which both the PS blocks and uncomplexed 2VP segments were soluble in THF, and CdS nanoparticles were stabilized by the P2VP chains. They then added these micelles to water with a low pH value. This caused the PS chains to collapse and the 2VP segments formed a complex with the acid. So a new micelle was created with a PS core and P2VP-H$^+$ complex corona. A source of S$^{2-}$ ions was added and CdS was formed within the corona of the micelle. They obtained randomly distributed CdS nanoparticles in the corona of the micelles resulting in a morphology similar to the “red currant” morphology described earlier and seen in Figure 2.13.
Figure 2.13 TEM image of corona-embedded CdS nanoparticles prepared by dropping 1 mL of the core-embedded CdS nanoparticle solution into 20 mL of water with a pH value of 3.3. Scale bars on the TEM images represent 100 nm.

For this study, the technique chosen for synthesizing the nanocomposite material will be the one employed by Tadd et al.\textsuperscript{28} This approach involved the one-step, \textit{in situ} incorporation of the metal nanoparticles into the desired domains of the block copolymer. For this technique, the metal precursor and the copolymer are made into a homogeneous mixture that is then heated. The metal precursor decomposes into the zero valent metal particles under an inert atmosphere, and self assembly takes place when solvent is removed. Figure 2.14 shows a TEM micrograph of a nanocomposite sample that was created using PS\textsubscript{25,300}-b-PMMA\textsubscript{25,900} as the copolymer and Co\textsubscript{2}(CO)\textsubscript{8} as the metal precursor.
As seen in Figure 2.14, the particles were mostly spherical in shape, and the researchers obtained an average particle size of 2nm. There are certain advantages to using this technique as compared to the previously described ones. In some of the previous techniques, the film is allowed to self assemble first, and then they are exposed to the metallic moiety. This creates a situation in which there can be a lot of variation in the size and distribution of the particles between the different regions in the film, caused by varying rates of diffusion and penetration depths of the metallic precursor into the film.

The techniques which used some type of salt reduction also had the drawback of having to remove excess byproducts from the solution after the reduction was complete. The chosen technique aims to avoid these issues by performing the nucleation and growth of the nanoparticles and the phase separation of the block copolymer in situ. In this case, nucleation and growth of the particles will be controlled both by kinetics and the interaction with the different blocks in the copolymer. This will allow us to take
advantage of the difference in reactivity between the metal nanoparticles and the copolymer blocks. This method is a truly *in situ* approach that allows for maximum interaction between the growing nanoparticles and the polymer chains, which is not the case for the other methods including the ones that can also be described as *in situ*.

As was mentioned previously, in order to synthesize a useful nanocomposite material for optical applications, certain conditions must be met. These materials must be periodic structures whose lattice constants are comparable to the wavelength of interest. There must also be alternating regions of high and low refractive index with an appreciable dielectric contrast between the regions. The first issue can be solved by using block copolymers which self-assemble into periodic structures. Despite the periodic nature of self-assembled block copolymers, the refractive index contrast between neighboring blocks is not sufficient for the material to be useful optically. Hence the second issue can be handled by preferentially sequestering metal nanoparticles into specific polymer domains so that there will be an increase in the refractive index contrast between neighboring blocks.

In order to optimize the synthesis of metal nanoparticle-polymer systems, there are certain processes which must be understood. Perhaps the most important one, which is the focus of this work, is the selective interfacial interaction between the block copolymer and the growing metal nanoparticles. To investigate this interaction, four different approaches will be taken. The first approach will be looking at the strength of interaction between the competing blocks of the copolymer and the metal nanoparticles surface. This will be done by looking at competitive adsorption between the homopolymers which make the chosen copolymer and the metal nanocluster surface. The second approach will look at the effect of polymer architecture on the metal nanoclusters.
Here the influence of block length and copolymer composition on the morphology of the metal nanoparticles will be investigated. The third approach will look at the polymer composition and solvent effects on the phase behavior of the metal nanocluster-block copolymer nanocomposite. Finally, the influence of the metal precursor on the rate of the decomposition will be examined. By combining the results from these four approaches, researchers will get a better understanding of the necessary conditions for tailoring the synthesis of metal-polymer nanocomposite materials using the in situ technique described earlier.
CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Overview

In this study, a true self-assembly method will be used in which the nucleation and growth of the nanoparticles, and the phase separation of the block copolymers will occur simultaneously and \textit{in situ}, in a homogeneous mixture of the two components. With these conditions, the polymer will act as a barrier to high mobility of the growing nanoclusters because of its viscosity, and the reactive block of the copolymer will act as the stabilizing element for the growing particles. Because of this, the nucleation and growth of the clusters will be dependent on the interaction with the available sites on the polymer chain, and not just reaction kinetics. This will allow the difference in reactivity of the two blocks toward the nanoparticle surface to be fully examined.

3.2 Competitive Adsorption of polymer on metal nanoparticles

For this phase in the study, toluene and cholorobenzene (spectral grade) were purchased from Fisher Scientific and were used without further preparation. The Polystyrene had a molecular weight of 100,000 g/mol (PDI = 1.04), and poly(methyl methacrylate) had a molecular weight of 120,000 g/mol (PDI = 1.06). The radius of gyration of both polymers is sensitive to the solvent, temperature and concentration: In the systems examined in this study Rg of both polymers is of order 60-70 Å.
3.2.1 Particle Synthesis

**Co-PMMA particles:** Forty-five mL of 6 wt% PMMA (120,000 g/mol) in chlorobenzene was added to a three-neck reaction flask, which had been evacuated and flushed with N₂ prior to solution introduction. Forty-five mL of a 1·10⁻² M solution of Co₂(CO)₈ in toluene was prepared and added to the same flask under a counter-current N₂ stream. A 1 mL sample of this solution was removed for FTIR analysis. The combined solution had a final concentration of 5·10⁻³ M Co₂(CO)₈ and 3 wt% PMMA. The solution was then heated under nitrogen for about 10 h at 90 °C in order to decompose the cobalt carbonyl complex by the removal of the CO groups, resulting in the formation of cobalt nanoclusters.¹⁷-²⁰ Note that the solvent composition for the Co-PMMA particles is approximately 1:2 chlorobenzene to toluene.

**Co in PS/PMMA mixtures:** The same decomposition procedure was followed starting with a polymer solution consisting of 3 wt% PS in toluene mixed with 3 wt% PMMA in chlorobenzene. In this case, the solvent composition is 1:6 chlorobenzene to toluene.

**Co-PS particles:** To obtain PS layers adsorbed on Co particles, forty-five mL of 6 wt% PS (100,000 g/mol) in toluene was added, as discussed above, to forty-five mL of a 1·10⁻² M solution of Co₂(CO)₈ in toluene to make a solution of 5·10⁻³ M Co₂(CO)₈ and 3 wt% PS. The solution was then heated under nitrogen for about 10 h at 90 °C in order to decompose the cobalt carbonyl complex into cobalt nanoclusters carrying adsorbed PS layers.¹⁷-²⁰ In this case, the solvent contains only toluene.

**Sequential adsorption:** Co-PMMA in PS was formed by adding twenty five mL of the decomposed particle solution to 25 mL of 3 wt% PS in toluene and incubated for ten days. The solvent composition in this case is therefore 1:6 chlorobenzene to toluene. Co-PS in PMMA was formed by adding twenty five mL of the decomposed particle solution
to 25 mL of 3 wt% PMMA in chlorobenzene and incubated for ten days. The solvent composition in this case is therefore 2:1 chlorobenzene to toluene. This case was also conducted in a solution of 1:1 chlorobenzene to toluene by mixing equal volumes of the Co-PS solution (toluene only) with PMMA in chlorobenzene.

3.2.2. Sample Characterization

Upon completion of the decomposition reactions (determined following the same procedures described elsewhere\textsuperscript{17-21}), transmission electron microscopy (TEM) samples were prepared by placing a drop of the solution onto a formvar-coated TEM grid. The grid was placed on top of a Kimwipe so that when a drop was placed onto the grid, the liquid was pulled through the grid leaving a thin film on top of the grid. The resulting samples were analyzed with a JEOL 100C TEM microscope having a resolution of 100kV. Electron diffraction patterns were used to identify the composition of the cobalt nanoparticles embedded in the polymer matrices. The PMMA-stabilized cobalt clusters contained a high fraction of cobalt oxides. Samples of the incubated solutions were also prepared using the same technique.

Samples for thermo-gravimetric analysis (TGA) were prepared by centrifuging aliquots of each solution to collect the polymer-coated particles. The particles were then washed repeatedly in pure solvent (either toluene or chlorobenzene) to remove excess loosely-bound polymer. The samples were analyzed with a TGA Q50 from TA instruments at a rate of 10 °C·min\textsuperscript{-1}. At this point, despite being handled in the atmosphere, the PMMA-stabilized cobalt clusters remained unchanged.
3.3 Effect of polymer architecture on the metal nanoclusters

For this phase, cyclohexanone, chlorobenzene (spectral grade), 2-ethoxy ethanol (spectral grade) and toluene (spectral grade) were purchased from Fisher Scientific and were used without further preparation. Block copolymers of PS-\(b\)-PMMA of varying molecular weights and varying compositions were purchased from Polymer Source Inc.: PS\(_{25300}\)-\(b\)-PMMA\(_{25900}\), PS\(_{71300}\)-\(b\)-PMMA\(_{11200}\), PS\(_{101100}\)-\(b\)-PMMA\(_{165800}\) and PS\(_{47000}\)-\(b\)-PMMA\(_{280000}\), with PDI ranging from 1.04 to 1.06. Homopolymers of PS and PMMA of various molecular weights were purchased from Alfa Aesar, with PDI values ranging from 1.04 to 1.12.

3.3.1. Particle Synthesis

Forty-five mL of 1 wt\% PS-\(b\)-PMMA in cyclohexanone, which is a common good solvent for both the PS and the PMMA blocks, was added to a three-neck reaction flask that had been evacuated and flushed with N\(_2\) prior to solution introduction. Forty-five mL of a 1·10\(^{-2}\) M solution of Co\(_2\)(CO)\(_8\) in cyclohexanone was prepared and added to the same flask under a counter-current N\(_2\) stream. A 1 mL sample of this solution was removed for FTIR analysis. The combined solution had a final concentration of 5·10\(^{-3}\) M Co\(_2\)(CO)\(_8\). The solution was then heated under nitrogen for about 10 h at 90 °C.

This same procedure was followed for the decomposition of Co\(_2\)(CO)\(_8\) in a solution of PS-\(b\)-PMMA in toluene, which is a preferential solvent for the PS block, or in 2-ethoxyethanol, which is a preferential solvent for PMMA.

Separately, control experiments were performed with both a solution of PS homopolymer alone (\(\bar{M}_w = 13,000 – 330,000\) g/mol) in toluene, and a solution of PMMA homopolymer alone (\(\bar{M}_w = 30,000 – 350,000\) g/mol) in chlorobenzene. Another control
experiment was performed with solutions of PMMA homopolymer alone ($M_w = 120,000 – 330,000 \text{ g/mol}$) in 2-ethoxy ethanol.

3.3.2. Sample Characterization

Upon completion of the decomposition reactions, transmission electron microscopy (TEM) samples were prepared by placing a drop of the solution onto a formvar-coated TEM grid. The grid was placed on top of a Kimwipe so that when a drop was placed onto the grid, the liquid was pulled through the grid leaving a thin film on top of the grid. The resulting samples were analyzed with a JEOL 100C TEM microscope having a resolution of 100 kV. The particles that were formed were mostly amorphous and consisted mainly of Co clusters with some traces of $\text{Co}_2\text{O}_3$ and CoO.
3.4 Polymer composition and solvent effects on the phase behavior of the metal nanocluster-block copolymer nanocomposite.

For this phase of the study, cyclohexanone, 2-ethoxy ethanol (spectral grade) and toluene (spectral grade) were purchased from Fisher Scientific and were used without further preparation. Block copolymers of PS-b-PMMA of varying molecular weights were purchased from Polymer Source Inc.

3.4.1. Particle Synthesis

Forty-five mL of 1 wt% PS\textsubscript{101,100}\text{-b-PMMA}\textsubscript{165,800} in cyclohexanone was added to a three-neck reaction flask, which had been evacuated and flushed with N\textsubscript{2} prior to solution introduction. Forty-five mL of a 1·10^{-2} M solution of Co\textsubscript{2}(CO)\textsubscript{8} in cyclohexanone was prepared and added to the same flask under a counter-current N\textsubscript{2} stream. A 1 mL sample of this solution was removed for FTIR analysis. The combined solution had a final concentration of 5·10^{-3} M Co\textsubscript{2}(CO)\textsubscript{8} and 0.5 wt% polystyrene. The solution was then heated under nitrogen for about 10 h at 90 °C. Similar experiments were performed with two other diblock copolymer compositions, in the same solvent and in the same solution concentration: PS\textsubscript{71,300}\text{-b-PMMA}\textsubscript{11,200} and PS\textsubscript{47,000}\text{-b-PMMA}\textsubscript{280,000}.

This same procedure was followed for the decomposition of PS\textsubscript{101,100}\text{-b-PMMA}\textsubscript{165,800} in toluene, which is a preferential solvent for the PS block. Finally, the above procedure was also followed starting with 45 mL of a 1wt% PS\textsubscript{101,100}\text{-b-PMMA}\textsubscript{165,800} in 2-ethoxyethanol, which is a preferential solvent for PMMA. Separately, two control experiments were performed with both a solution of PS homopolymer alone (\(\bar{M}_w = 25,000\) g/mol) in toluene, and a solution of PMMA homopolymer alone (\(\bar{M}_w = 30,000\) g/mol) in 2-ethoxyethanol.
3.4.2. Sample Characterization

Upon completion of the decomposition reactions, transmission electron microscopy (TEM) samples were prepared by placing a drop of the solution onto a formvar-coated TEM grid. The grid was placed on top of a Kimwipe so that when a drop was placed onto the grid, the liquid was pulled through the grid leaving a thin film on top of the grid. The resulting samples were analyzed with a JEOL 100C TEM microscope having a resolution of 100kV. The particles that were formed are mostly amorphous and consist mainly of Co clusters with some traces of $\text{Co}_2\text{O}_3$ and CoO.
3.5 Effect of initial $\text{Co}_2(\text{CO})_8$ concentration on the rate of decomposition reaction

For this study, chlorobenzene (spectral grade) were purchased from Fisher Scientific and were used without further preparation. Polystyrene with a molecular weight of 100,000 g/mol (PDI = 1.04) was purchased from Research Chemicals Ltd., and poly(methyl methacrylate) with a molecular weight of 120,000 g/mol (PDI = 1.06) was purchased from Aldrich Chemical Co.

3.5.1. Particle Synthesis

**Co-PMMA particles:** Forty-five mL of 6 wt% PMMA (120,000 g/mol) in cyclohexanone was added to a three-neck reaction flask, which had been evacuated and flushed with N$_2$ prior to solution introduction. Forty-five mL of a $1 \cdot 10^{-2}$ M solution of $\text{Co}_2(\text{CO})_8$ in cyclohexanone was prepared and added to the same flask under a counter-current N$_2$ stream. A 1 mL sample of this solution was removed for FTIR analysis. The combined solution had a final concentration of $5 \cdot 10^{-3}$ M $\text{Co}_2(\text{CO})_8$ and 3 wt% PMMA. The solution was then heated under nitrogen for about 10 h at 90 °C in order to decompose the cobalt carbonyl complex by the removal of the CO groups, resulting in the formation of cobalt nanoclusters. This procedure was repeated by subsequently increasing the $\text{Co}_2(\text{CO})_8$ concentration to two, three and four times the original value.

**Co-PS particles:** To obtain PS layers adsorbed on Co particles, forty-five mL of 6 wt% PS (100,000 g/mol) in cyclohexanone was added, as discussed above, to forty-five mL of a $1 \cdot 10^{-2}$ M solution of $\text{Co}_2(\text{CO})_8$ in cyclohexanone to make a solution of $5 \cdot 10^{-3}$ M $\text{Co}_2(\text{CO})_8$ and 3 wt% PS. A 1 mL sample of this solution was removed for FTIR analysis. The solution was then heated under nitrogen for about 10 h at 90 °C in order to decompose the cobalt carbonyl complex into cobalt nanoclusters carrying adsorbed PS.
layers. This procedure was repeated by subsequently increasing the Co$_2$(CO)$_8$ concentration to two, three and four times the original value.

### 3.5.2. Sample Characterization

Upon completion of the decomposition reactions, transmission electron microscopy (TEM) samples were prepared by placing a drop of the solution onto a formvar-coated TEM grid. The grid was placed on top of a Kimwipe so that when a drop was placed onto the grid, the liquid was pulled through the grid leaving a thin film on top of the grid. The resulting samples were analyzed with a JEOL 100C TEM microscope having a resolution of 100kV. The particles that were formed are mostly amorphous and consist mainly of Co clusters with some traces of Co$_2$O$_3$ and CoO. FTIR analysis was also done to determine the rate of the decomposition reaction in each polymer system.

First, a spectrum was taken of the polymer solution without Co$_2$(CO)$_8$ present. After addition of the Co$_2$(CO)$_8$ solution to the polymer solution, and mixing for about 1 minute, another spectrum was taken of the undecomposed solution. Spectra were then recorded in regular intervals for the duration of the reaction. In order to take a spectrum, an aliquot of the sample was placed into a demountable infrared cell using KBr windows. The reaction flask was pressurized with nitrogen to prevent oxidation of the particles. The cell was washed after each sample collection with pure solvent. This procedure was followed for taking spectra at each subsequent Co$_2$(CO)$_8$ concentration.
3.6 Characterization Techniques

3.6.1 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a useful technique in the characterization of nanocomposite samples. The transmission electron microscope (TEM) uses some of the same basic principles as the light microscope but with electrons as the “light source”. Since the TEM uses electrons to probe the sample and electrons have a lower wavelength, it is possible to better much better resolution than a light microscope can attain. The TEM can provide magnification of more than 100,000 times the actual size of the features in the sample, and thus can provide a lot of information about the material that other methods can not provide. It has been found that the resolution that can be obtained for polymer samples lies between 1-100 nm, which is adequate for this study.

One of the biggest obstacles to TEM lies in the fact that the samples must be thin, and able to withstand a focused electron beam. Thus the sampling method becomes very important. The TEM is made up of an electron source, a series of condenser lenses, a specimen holder, an objective lens, intermediate and projector lenses, and finally a phosphor screen that the image appears on. Most of the sources are thermionic guns which produces a stream of monochromatic electrons. The beam of electrons then passes through a condenser system that removes the high angle electrons and focuses the beam. The beam continues down the TEM and strikes the specimen where parts of it are further transmitted. The transmitted part of the beam is focused by the objective lens into an image. The image passes through a column of intermediate and projector lenses which enlarges the image. Finally the image strikes the phosphor screen and light is produced, which allows the image to be seen. There are certain factors which can reduce the resolving power of the TEM. These include spherical aberrations like distortion, lens
asymmetry that leads to images that are not sharp, and chromatic aberrations that result from electrons having different wavelengths. All of these factors can be mitigated to a certain degree by changing the configuration of some of the components within the TEM itself. In this work, TEM will be used primarily to gather information about the shape, size and distribution of the cobalt nanoclusters within the various polymeric matrices. The electron diffraction component of the TEM will also be used to obtain information about the crystal structure of the nano-sized particles.

3.6.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique that studies the weight change of a particular specimen as a function of the temperature applied. The data obtained from a TGA can be used to study the degradation temperature of materials like polymers, the absorption or evolution of gases at high temperatures, and it has also been used to look at the decompositions of clay filler in some polymer composite materials. The balance used in TGA devices are very sensitive and some have resolutions down to 1 µg. In the typical TGA, the specimen is placed into a refractory pan that is made usually of platinum or porcelain. The pan is then placed into the hot zone of the machine and suspended from a high precision balance. For temperature measurements, a thermocouple is placed in close proximity to the specimen but not touching it so that it does not interfere with the free float of the balance. In some designs a flag is located beneath the balance arm that interferes with infrared light coming from a source to a detector. A feedback mechanism adjusts the current in the coil and by extension the position of the flag, in order to keep constant illumination at the detector. The current sent to the coil to keep the flag at a constant position is proportional to the weight loss or gained by the
material. By continuously monitoring this process, a thermogram is obtained which shows the weight loss or gained as the temperature increases. This technique will be used to analyze the polymer composition on the surface of the nanoparticles.

3.6.3 Fourier Transform Infrared Spectroscopy (FTIR)

All organic molecules reside in a particular energy level at the ground state. This ground state could be changed by absorption of electromagnetic radiation. It is the bonds in the molecules which absorb this radiation, and only at specific frequencies. In this technique, the source produces light in the infrared region that strikes the specimen. Infrared radiation is not strong enough to cause excitation of electrons in the species, but it does cause the atoms of organic compounds to vibrate about the covalent bonds that connect them. The functional groups present in organic compounds are arranged in a specific manner and absorption of IR radiation by these molecules will occur in a way that is characteristic of the type of bonds in that molecule. This is another way of saying that the vibrations are quantized and when they occur, the compounds absorb IR energy in a specific region of the IR spectrum. An IR spectrometer operates by sending an IR beam through the sample and comparing the transmitted radiation through the sample with that in the absence of the sample. Any absorbed frequencies will be evident by the difference. The device then plots this result showing absorbance versus wavenumber. In this work, FTIR will be used to monitor the decomposition of Co$_2$(CO)$_8$ into cobalt clusters in the polymeric matrix. It will also be used to study the kinetics of the decomposition reaction both in PS and PMMA. This will be done monitoring the change in height of two peaks associated with bridging carbonyls in octacarbonyl dicobalt. These peaks are located at 1858 cm$^{-1}$ and 1867 cm$^{-1}$. These peaks were chosen because: 1)
Co$_2$(CO)$_8$ is made up of three isomers whose relative concentrations are dependent on reaction conditions. Two of the three isomers do not have bridging carbonyls, which means that the 1858 peak belongs to the bridging isomer only. The concentration of the bridging isomer is known for every temperature, and thus changes in the 1858 band may be directly correlated to the concentration of Co$_2$(CO)$_8$. The 1867 band represents the bridged Co$_4$(CO)$_{12}$ isomer and thus changes in its intensity can be taken to reflect changes in the absolute concentration of this species.
CHAPTER 4

COMPETITIVE ADSORPTION OF POLYMER ON METAL NANOPARTICLES

4.1 Overview

In order to design and synthesize a nanocomposite material based on a block copolymer metal nanoparticle system, one must understand the types and strengths of interactions which takes place between the constituent blocks of the copolymer and the surface of the metal nanoparticles. This relationship is important since many of the properties of the new composite material will be based on the location and type of dispersion of the nanoparticles within the polymer matrix.

The adsorption of polymeric chains onto various substrates has been studied extensively in the past decade.\textsuperscript{30-37} The process is governed by a competition between the adsorption energy per polymer segment in contact with the substrate, the loss of configurational entropy due to chain confinement on the surface, and the interactions between the polymer and the solvent.\textsuperscript{30,36-38}

Several studies\textsuperscript{39-41} examined the displacement of adsorbed polymer chains by other polymer species. In general, shorter chains may be displaced by longer chains due to the fact that longer chains have more “adsorption sites” (i.e. segments) per chain and incur less configurational entropy loss upon adsorption. Adsorbed polymer chains may be displaced by other chains of similar molecular weight if the adsorption energy of the substituting chains is stronger.\textsuperscript{41} However, it should be emphasized that the strength of the adsorption energy is not an absolute value, but is relative to the strength of polymer-
solvent interaction. In general, polymer adsorption leads to the formation of a dense layer where the number of polymer/polymer contacts is increased, and the number of polymer/solvent contacts decreases. Thus, polymers immersed in a poor solvent will strongly adsorb to a surface that is only weakly compatible (or even incompatible) to reduce interactions with the unfavorable solvent, while polymers in a good solvent are less likely to adsorb even onto a strongly compatible substrate.\textsuperscript{42-45} Polymer adsorption and displacement has also been shown to be sensitive to the concentrations of the polymeric species (a small concentration of strongly adsorbing polymer may not displace a high concentration of weakly adsorbing polymer).\textsuperscript{42-45} The effect of all these parameters may be lumped into the chemical potential of the polymeric species.\textsuperscript{42-45}

In order to test the extent of interaction, which is the driving force for the incorporation of metal nanoparticles within the polymer domains, we will first examine competitive adsorption of a strongly adsorbing polymer and a weakly adsorbing polymer on metal nanoparticles. In this scenario, there are three possible outcomes as illustrated by the following figure:
If adsorption of the strongly interacting PMMA (red) block dominates, then the sequential adsorption of PMMA (red) followed by the addition of PS (blue) should yield the same result as that obtained from adsorption from a PMMA/PS mixture, namely, an adsorbed layer on the nanoparticle consisting only of PMMA (Figure 4.1a). If coadsorption of the two polymers is favored, then both routes should produce a mixed layer consisting of PS and PMMA (Figure 4.1b). Finally, if the strongly adsorbing PMMA forms a non-equilibrium layer that cannot be displaced, but equilibrium favors mixed layers, then sequential adsorption would lead to PMMA only layers, while adsorption from a mixture would lead to mixed layers (Figure 4.1c).

This particular investigation will help provide insight into the behavior of nanoparticle distribution within the domains of block copolymer systems containing constituent blocks of varying chemical reactivity. It could also lead to a procedure to actually tailor these nanocomposite materials based on each block’s affinity to the nanoparticle. We find that, as in the case of adsorption on flat substrates, the solvent quality plays a crucial role in determining the adsorbed layer properties. Using thermal...
gravimetric analysis (TGA), we show that the adsorbed layer contains only the strongly interacting polymer, regardless of the adsorption sequence, if the solvent is a common good solvent for the two polymeric species. However, if the solvent is poor for the weakly interacting species, it remains on the particle so that the adsorbed layer is composed of both polymers.

4.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a particularly useful tool when dealing with nanoparticulate and colloid science. This technique allows the researcher to obtain valuable information about the system being studied including size, shape and distribution of the nanoparticles. In this study we used this technique to image samples obtained from the thermal decomposition of the cobalt precursor in the presence of different polymer systems.

The TEM micrographs of cobalt nanoparticles formed in the presence of polystyrene alone and subsequently after incubation in a solution containing poly(methyl methacrylate), are shown in the following figures:
Figure 4.2 TEM of a) Co-PS system and b) Co-PS incubated in PMMA system
In the case of the cobalt-PS system (Figure 4.2a), there is evidence of particle flocculation, giving rise to small chains and star-like particles. On the other hand, when the same system was further incubated with PMMA, the flocculation seemed to break, leaving mostly individual particles in the system (Figure 4.2b). The calculated fraction of flocculated particles in the cobalt-PS system is high, $\frac{N_f}{N_{tot}} \geq 0.9$ (where $N_f \geq 3$ is the number of particles present in a flocculate with three or more basic particles, and $N_{tot}$ is the total number of basic particles, as evidenced from the TEM images shown in Figure 4.2, while the majority of particles in the cobalt-PS system that has been incubated with PMMA are either single particles, or are present as dimers and to a much lesser extent as trimers,

$\frac{N_f}{N_{tot}} \leq 0.1$, as shown in Figure 4.3

![Histogram showing number of particles per floc in Cobalt-polymer systems](image)

**Figure 4.3** Histogram showing number of particles per floc in Cobalt-polymer systems
This suggests that the PMMA forms a layer that adsorbs onto the Co-PS complex, thereby breaking the flocculates and adding steric stabilization.

4.3 Electron Diffraction Studies

Using the TEM, electron diffraction studies were also performed on the nanocomposite samples. This technique allowed us to determine the crystal structure of the nanoparticles that were synthesized, in order to see if there is a difference in the crystal structure of the bulk cobalt.

![Figure 4.4 Electron diffraction patterns of a)Co-PS and b)Co-PS in PMMA](image)

**Figure 4.4** Electron diffraction patterns of a)Co-PS and b)Co-PS in PMMA
Using the camera equation, \( r/L = \lambda/d \), where \( r \) is the ring radius obtained on the diffraction pattern, \( L \) is the camera length, \( \lambda \) is the wavelength of the electron beam used and \( d \) is the interplanar spacing. For the Co/PS system, the calculated value of \( a \) is \( 3.25 \times 10^{-10} \) m. The measured value for fcc Co is \( 3.54 \times 10^{-10} \) m. The calculated value is different by 8%, which is within an acceptable range. Therefore it can be concluded that the nanoparticles obtained were fcc Co, a deviation from the hcp bulk structure.

For the Co/PS/PMMA system, the calculated value of \( a \) is \( 3.07 \times 10^{-10} \) m. The measured value for fcc Co is \( 3.54 \times 10^{-10} \) m. The calculated value is different by 13%, which is within an acceptable range. Therefore it can be concluded that the nanoparticles obtained were fcc Co, a deviation from the hcp bulk structure.

The following table shows further analysis done on the diffraction patterns using radius ratios of the diffraction pattern.

**Table 4.1 Calculated d spacing of Co in nanocomposite samples**

<table>
<thead>
<tr>
<th>Co-PS System ( R ) (cm)</th>
<th>d-spacing (nm)</th>
<th>Compound</th>
<th>Co-PMMA System ( R ) (cm)</th>
<th>d-spacing (nm)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>1.62</td>
<td>Co(_2)O(_3)</td>
<td>2.0</td>
<td>1.54</td>
<td>Co(_2)O(_3)</td>
</tr>
<tr>
<td>3.3</td>
<td>0.93</td>
<td>( \alpha )-Co</td>
<td>3.4</td>
<td>0.90</td>
<td>( \alpha )-Co</td>
</tr>
<tr>
<td>5.9</td>
<td>0.52</td>
<td>CoO</td>
<td>4.3</td>
<td>0.71</td>
<td>CoO</td>
</tr>
</tbody>
</table>

From these results, one can see that the PS-stabilized cobalt clusters consisted mainly of \( \alpha \)-Co, while the PMMA-stabilized cobalt clusters contained a higher fraction of cobalt oxides.
4.4 Atomic Force Microscopy

Atomic Force Microscopy was used to study the morphology of the thin films created from samples of each nanocomposite system. The following are the resulting AFM pictures:
AFM images of the Co-polymer particles are shown in Figure 4.5. In Co-PMMA systems (Figure 4.5a), the micrograph shows the cobalt particles homogeneously distributed on the surface. This type of distribution remained even after these particles were incubated in PS solutions (Figure 4.5b). Finally, when the synthesis of the cobalt particles was conducted in a solution containing equal concentrations of both PS and PMMA (Figure 4.5c), the observed particle distribution in the film is similar to the homogeneous dispersion found in the other systems containing PMMA. Despite the fact that the Co-PMMA particles have only a PMMA adsorbed layer while the other two systems have a PMMA and PS co-adsorbed layer, the amount of PMMA on the surface in all three system was sufficient for the effective stabilization of the cobalt particles.
Figure 4.6 AFM images of thin samples of a) Co-PS system, b) Co-PS incubated in PMMA
AFM images of thin film samples resulting from the cobalt-PS system shown in Figure 4.6, is expected to exhibit considerable surface roughness due to the flocculation of the cobalt basic particles. Indeed, this system shows ridges on the surface of the sample, corresponding to particle chains (Figure 4.6a). Upon subsequent incubation in PMMA (Figure 4.6b), the surface of the sample became more homogeneous and the ridges have disappeared. This observation is a result of the break-up of the cobalt chains found in the PS-only system, by reversing the flocculation process and generating a majority of individual or dimer particles. These results are consistent with the increase in the density of the PS adsorbed chains due to their collapse upon the introduction of the PMMA/chlorobenzene solution, and the subsequent formation of a PMMA ad-layer on top of the PS film. The newly formed collapsed dense PS layer would be capable to overcome the van der Waals attraction between the cobalt particles and allow the breakdown of the flocculates.

4.5 Thermogravimetric Analysis (TGA)

The goal of this study is to examine competition and displacement in polymer layers adsorbed on nanoparticles, as a function of the solvent properties and the sequence of adsorption. Since polymer adsorption is sensitive to the interface curvature, the nanoparticles used must be uniform in size, resist flocculation. Moreover, no traces of surface-active agents such as surfactants must be present, to avoid interference with the polymer adsorption process.

The procedure utilized here is a method previously developed for the synthesis of metal nanoparticles in polymeric suspensions.\textsuperscript{38,46-50} The method yields monodisperse metal particles, which are covered by an adsorbed layer of the polymeric species.\textsuperscript{38} Thus,
Co nanoparticles formed in a PMMA suspension will be covered by an adsorbed PMMA layer, while those formed in a PS suspension are covered by an adsorbed PS layer.

![Figure 4.7](image.png)

**Figure 4.7** The particle size distribution, as determined by TEM for particles used in this study.

Figure 4.7 shows a plot of the dimensions of the different particles used in this study, as characterized by TEM and AFM. Co-PS denotes Co particles synthesized in PS solutions, and thus carrying an adsorbed PS layer. Co-PMMA is particles synthesized in PMMA solutions, and Co+PS+PMMA particles formed in a mixed polymer solution. Co-PMMA+PS denotes particles initially carrying a PMMA layer that are subsequently immersed in a solution of PS chains, and Co-PS+PMMA particles initially immersed in PS and subsequently put in PMMA solutions.

It was seen that, regardless of the polymer suspension properties, the particle size is similar, of order 15-20 nm, and the size distribution as given by the range of sizes (see error bars) is relatively narrow. Subsequent processing (e.g. immersion in another polymeric solution) does not affect the particle size.
Understanding competitive adsorption requires a methodology for probing the adsorbed layer characteristics. The thermal degradation of adsorbed polymers is directly related to the strength of the interaction between the polymer chains and the substrate, and, to a lesser degree, the film thickness.\textsuperscript{51-54} Thus, the degradation profile of a polymer mix (whether in bulk or on a substrate) where there are no specific bonds between the polymeric species is given by the appropriately weighted profile of the components.\textsuperscript{51-54} The TGA profile of PS and PMMA mixtures follow this rule, as recently shown by Chuai et al.\textsuperscript{55} who show that the TGA profile of blends ranging from 0-100% PS can be decomposed into the weighted average of the two components.

PS is known to undergo one, relatively sharp transition which corresponds to the dissociation of C–C bonds along the polymer main chain resulting in chain scission, as shown in Equation 1.\textsuperscript{52,53,56-57}
As a reference, free PS thin films were made, and the TGA of those films are shown in Figure 4.8. These films were ~ 10 µm and the decomposition was seen to occur at approximately 400 °C.

![Figure 4.8 TGA trace of thin PS film](image)

In comparison, the TGA profile of PS adsorbed onto Co particles shows the main decomposition transition at a lower temperature of approximately 347 °C, as can be seen in Figure 4.9.
When viewed together, it can be seen that the shape of the two profiles is similar, indicating that in both films the decomposition transition follows the mechanism of Equation (1). The reduction in the main chain scission temperature of PS is due to the effects of film thickness: The thickness of the adsorbed film is of order \( \sim 5 \text{ nm} \),\(^{38}\) orders of magnitude smaller than the thickness of the reference film, thereby leading to a lower
transition temperature. Indeed, in true bulk systems, PS undergoes the scission transition at approximately 430 °C (Figure 3.a).\textsuperscript{58}

Bulk PMMA films are known to undergo \textit{two} main transitions.\textsuperscript{58-60} The first transition is centered at 282 °C and corresponds to the dissociation of the methoxy group on the acrylic side chain, as shown in Equation 2:

\begin{equation}
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{CH}_3 \\
\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{CH}_3 \\
\text{C} \\
\text{O} \\
\text{H}_2 \\
\text{C} \\
\text{CH}_3 \\
\end{array}
\end{equation}

The second transition is centered at 376 °C and corresponds to dissociation of C–C bonds along the polymer main chain resulting in chain scission, as shown in Equation 3:

\begin{equation}
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{CH}_3 \\
\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{C} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{H}_2 \\
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{CH}_3 \\
\text{H}_2 \\
\end{array}
\end{equation}
In Figure 4.11, the TGA profile PMMA films was examined. It was seen that the free PMMA thin film of ~ 10 µm displays the two transitions. The dissociation of the methoxy group on the acrylic side chain (Equation 2) is shifted to a lower temperature of approximately 275 °C, while the main-chain scission remains at approximately 375 °C (see inset). In the case of a thin PMMA film (~5nm) adsorbed on Co nanoparticles, the side-chain transition is more or less completely suppressed (see inset), but the main-chain scission transition remains, as in the bulk and moderately-thick films, at the approximate value of 375 °C.

Figure 4.11 Combined TGA of PMMA systems
Figures 4.10 and 4.11 clearly show that TGA measurements are an effective methodology to probe the polymer film adsorbed on Co particles. In Figure 4.12, TGA profiles of PMMA adsorbed on Co nanoparticles with that of Co-PMMA particles that were immersed, after formation, in a PS solution, Co particles in a mixture of PMMA and PS, and Co-PS particles that were immersed in a PMMA solution were compared. The competitive adsorption and sequential adsorption experiments were conducted in a mixed solvent containing chlorobenzene (a selective solvent for PMMA, namely, a good solvent for PMMA but poor for PS) and toluene (common good solvent) at ratios varying from 1:1 to 1:6.

Figure 4.12 shows that the TGA profile is identical for the sequential adsorption (namely, one polymer and then the other) as well as for the competitive adsorption (mixing both polymers in solution). The profile is similar to that of PMMA films adsorbed on Co nanoparticles, thereby suggesting that the films formed during competitive or sequential adsorption are composed of practically only PMMA.
Figure 4.12 TGA profile of sequential and co-adsorption in a common good solvent. The line denotes Co-PMMA, (o) Co in PMMA/PS mixtures, (+) Co-PMMA followed by PS, and (x) Co-PS followed by PMMA. We see that all profiles are similar, thereby indicating the adsorbed layers formed in all cases are predominantly composed of PMMA.

To examine the effect of the solvent on sequential adsorption, Co-PS particles immersed in a PMMA solution, when the solvent composition was 1:1 and 1:6 chlorobenzene to toluene was compared (Figure 4.13). It was seen that the two cases play significantly different TGA profiles, thereby suggesting that the composition of the adsorbed layer formed in the 1:1 solvent mixture differs from that of the mostly toluene one.
In this phase of work, the effect of sequential vs. co-adsorption of polymers on Co nanoparticles was investigated. The structure and properties of adsorbed polymer layers are sensitive to the interface curvature, as defined by the ratio between the chain radius of gyration and the substrate radius of curvature. When adsorption of polymer chains occurs on the surface of nanoparticles rather than on flat surfaces, the high interfacial curvature of the particles imposes constraints on the configurations of the adsorbing chains. As a result the fraction of the surface sites occupied by an adsorbed chain segment decreases with decreasing particle radius.
Due to the sensitivity of the adsorbed layer properties to particle dimensions, examining polymer adsorption on nanoparticles requires that the particles be uniform in size and resist flocculation; size polydispersity or aggregation may affect the adsorption process and complicate analysis. In this study we use Co nanoparticles that were synthesized in situ in the polymer suspension,46-50 a method that has been shown to yield monodisperse populations of particles that are sterically stabilized against flocculation.46-50. The adsorbing polymers consist of polystyrene (PS) and poly(methyl methacrylate) (PMMA). Since, as discussed earlier, chain MW plays a role in polymer adsorption and displacement, the polymers used had similar molecular weights, number of adsorbing units and radius of gyration in good solvent (Rg ~ 6-7 nm). However, they differ in the nature and strength of their interactions with metal substrates: PS is known to adsorb onto Co surfaces through weak dipole-dipole interactions involving the π-electrons of the pendant benzene ring and the relatively positive reactive cobalt surface sites.61-65 The reduction of surface energy per segment as a result of the polymer chain adsorption on the surface of cobalt clusters is roughly 1.5 kcal/mole.66-69 PMMA is known to interact through the coordination of the carbonyl groups on the acrylate side group with the reactive cobalt surface sites,70, 71 resulting in a relatively strong bond. The reduction of surface energy per segment as a result of the polymer chain adsorption on the surface of cobalt clusters is roughly 7.5 kcal/mole, namely, five times the strength of the PS-Co binding66-69 illustrated in Figure 4.14
It was found (see Figure 4.10) that in the case of PS films, the main scission temperature decreases consistently with decreasing film thickness. In PMMA, the film thickness does not significantly affect the main-chain scission transition, which remains at the same value as in bulk PMMA\textsuperscript{58-60} for both the moderate film of 10\,µm, or the thin film adsorbed on Co nanoparticles. However, adsorption onto Co particles suppresses the side-chain transition (Figure 4.11 inset). We suggest that this stabilization of the side–chains against scission arises from the coordination of the carbonyl groups on the acrylate side group with the reactive cobalt surface sites\textsuperscript{70,71}.

The TGA profiles of the two polymers adsorbed on the Co nanoparticles differ significantly, thereby enabling us to probe the composition of the adsorbed films in cases of competitive or sequential adsorption. As shown in Figure 4.12, we find that the order of adsorption (PS and then PMMA, PMMA and then PS, or adsorption from a mixture) does not affect the composition of the adsorbed layer in systems where the mixed solvent is good for both polymers (namely, the cholorobenzene content is lower than \(~50\%\)). In these cases, the adsorbed layer is dominated by PMMA. This is in agreement with the
fact that PMMA strongly interacts with Co surfaces (an interaction strong enough to suppress the side-chain scission), while PS interacts only weakly with these surfaces.

However, the predominance of PMMA in the adsorbed layer depends on the solvent quality: In Figure 4.13, PS layers adsorbed on Co nanoparticles that were immersed in a solution of PMMA were examined. Comparing the TGA profile of the adsorbed layer in a solvent that is good for both polymers (1:6 chlorobenzene to toluene) to that obtained in a selective solvent that is poor for PS (2:1 chlorobenzene to toluene), one can see that composition of the adsorbed layer differs significantly. While in the common good solvent PMMA displaces the adsorbed PS completely, this is not the case in the selective solvent. In fact, one finds that the TGA profile of the adsorbed layer in the latter case can be approximated by a linear superposition of the Co-PS and PMMA film profiles, suggesting that the adsorbed film contains 55% PS, and 45% PMMA. The fact that a significant amount of PMMA could adsorb onto the nanoparticles is interesting, since it might be expected that the PS would form a dense impenetrable layer around the nanoparticles, thereby inhibiting access to the Co surface. The formation of the mixed adsorbed layer indicates that PS does not saturate all surface sites, i.e. a large fraction of them remains available. This is in agreement with our earlier analysis, which finds that the number of occupied surface sites on nanoparticles is very low when compared to large/flat surfaces.

The effect of the solvent quality on the composition of the adsorbed layer can be understood in terms of the chemical potential, or free energy, of the adsorbing polymers. In a common good solvent, the free energy of either polymers is low; the adsorbing species is then the one with the strongest affinity to the surface, namely, PMMA. However, in a selective solvent, the free energy of a poorly-solvated polymer (PS) can be
reduced via adsorption. Thus, it is harder to displace by the strongly-interacting polymer.\textsuperscript{72-75}

In conclusion, it was found that the adsorption of polymers on nanoparticles depends on the strength of the polymer-substrate interactions and the solvent quality. A strongly-interacting polymer will displace a weakly-interacting one only if the solvent is a good (or moderate) solvent for the latter. In a poor solvent, weakly interacting polymers cannot be displaced, but due to the availability of ‘free’ surface sites co-adsorption is possible, thus leading to the formation of a mixed adsorbed layer.
4.6 SUMMARY

In this phase of research we investigated the effect of system properties and adsorption sequence on competitive adsorption of poly(methyl methacrylate) (PMMA) and polystyrene (PS) on monodisperse cobalt (Co) particles (R ~ 15 nm). The adsorbed layer composition was studied using thermo-gravimetric analysis (TGA). We found that adsorbed layers of PS are completely displaced by PMMA when the solvent is a common good solvent. An adsorbed layer of only PMMA is also obtained through competitive adsorption from a common good solvent. However, in a selective solvent that is poor for PS, sequential adsorption leads to the formation of mixed layers.
CHAPTER 5

EFFECT OF POLYMER ARCHITECTURE ON THE COBALT NANOCLUSTERS

5.1 Overview

Another important aspect that must be considered when synthesizing these nanocomposite materials is the influence of polymer block length on the size of the particles. Being able to fully control the size of the nanoparticles is important since so many potential technological applications of these nanocomposite materials rely on the ability to synthesize particles of specific size and size distribution. For example, materials which take advantage of the quantum size effects, or which are used for opto-electronic applications, will employ small nanoparticles that have a fairly narrow size distribution range. Single crystals in the nano-regime are also important when designing materials that can be used as catalysts, and finally stable nanosized agglomerates also exhibit catalytic and optical properties. Thus control of size is very important to the overall performance of the nano-composite material.

As nanoparticles are placed within a polymer matrix, attention must be paid to the amount of intensity loss due to scattering when light passes through these materials. It has been found that the intensity loss can be estimated with the following equation:

$$I/I_o = e^{-\left[3\phi pr^3/4\lambda^4 \left( \frac{n_p}{n_m} - 1 \right) \right]}$$

Where $r$ is the radius of the spherical particle with refractive index $n_p$, dispersed in a matrix with refractive index $n_m$, $I$ is the intensity of the transmitted light, and $I_o$ is the intensity of the incident light, $\phi_p$ is the volume fraction of the particles dispersed in the matrix, $\lambda$ is the wavelength of light, and $x$ is the length of the optical path.
The above figure shows the transmittance as a function of the particle radius for a series of particles with varying refractive indices. In this plot, it can be seen that there is significant scattering when the particle radius goes above 50nm. Regular composites which contain polymers and inorganic particles in the µm regime are normally opaque in nature unless the refractive index of the matrix and filler are equal. So the use of polymer composites filled with nanoparticles with radii below 50 nm would be very desirable in many optical applications because of the negligible loss due to scattering.

One of the more unique features of nanostructured materials is the sensitivity of properties such as chemical activity, mechanical moduli or optical response to the (nano) domain size. This feature may be utilized to ‘tune’ the material performance through manipulation of the nanodomain size and spatial distribution. However, due to the strong correlations between domain size and material properties, even a small degree of polydispersity in domain size may affect the material performance.
Recent studies have shown that conducting the synthesis of inorganic nanoclusters in polymeric media (either bulk/melt or solution) yields narrow size and morphology distributions and suppresses cluster flocculation. The most important parameter controlling the nanocluster size has been found to be the polymer chemistry. The size of nanoclusters formed in polymeric melts where no solvent is present was shown to be independent of polymer molecular weight and the inorganic component volume fraction. Clusters formed in polymeric solutions were shown to vary in size as a function of the chain molecular weight or concentration. It has been suggested that the polymer controls the nanocluster size through equilibrium ‘capping’, although recently we have shown that the narrow size distribution may be due to the kinetics of nucleation and growth in polymeric suspensions.

Selective doping of diblock copolymer domains with inorganic nanoclusters may be used to obtain spatially ordered nanocomposites with high refractive index contrast between the domains for optoelectronic applications. It has been recently shown that metal nanoclusters synthesized in situ in diblock copolymer matrices selectively partition into the polymeric phase that has a higher affinity for the particles. As a result, in situ synthesis of inorganic nanoparticles in diblock copolymers is a promising method for obtaining spatially ordered, selectively doped nanocomposites.

The goal of this phase of research is to determine the effect of polymer structure and microdomain formation on the size of metal nanoclusters synthesized in situ by comparing clusters formed in homopolymer solutions to those obtained in diblock copolymer suspensions. The focus is on the effect of polymer molecular weight, composition and solvent properties on the size and size distribution of the nanoclusters. The metal particles examined are Co nanoclusters, obtained from the
decomposition of Co$_2$(CO)$_8$. The polymeric species include polystyrene (PS) and poly-
methyl methacrylate (PMMA) homopolymers, and PS-PMMA diblock copolymers and
the results of all experiments are summarized in Table 5.1.

**Table 5.1** Summary of the various experiments performed with both PS-PMMA diblock
copolymers and PS and PMMA homopolymers

<table>
<thead>
<tr>
<th>PMMA MW (g/mol)</th>
<th>PS MW (g/mol)</th>
<th>MMA weight %</th>
<th>Solvent</th>
<th>Overall MW (g/mol)</th>
<th>Cluster size (nm)</th>
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<tr>
<td>11,200</td>
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<td>62.1</td>
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<td>32</td>
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</table>

* Identical experiment performed also in 2-ethoxy ethanol, another good solvent for PMMA, yielding similar average cluster size.
In these experiments, cyclohexanone is a common good solvent for both PS and PMMA; Toluene is a good solvent for PS; 2-ethoxy ethanol and chlorobenzene are good solvents for PMMA. Polymers with various molecular weights (MW) were also used. As in previous studies, the distribution in cluster size is found to be narrow, with a polydispersity of order 10% or less. It should be noted that the error in cluster size is due to the presence of clusters that are either smaller or larger than the average size, thereby suggesting a kinetic control mechanism.

5.2 Effect of homopolymer MW on the Co cluster size

In Figure 5.2, the size of Co clusters formed in the two homopolymers, PS and PMMA, as a function of the chain molecular weight was examined. The solvents used (toluene for PS and chlorobenzene for the PMMA) are known to be good solvents for their respective polymers at the temperature range of the experiment (~90 °C).

Figure 5.2: The effect of homopolymer MW on the Co cluster size. Triangles denote PMMA in chlorobenzene and circles PS in toluene; the solvents are good solvents for their respective polymers under the synthesis conditions.
It was found that, in both types of homopolymer suspensions, the cluster size is minimal at a finite chain molecular weight, at approximately 200,000 g/mol for the PMMA solutions, and 100,000 g/mol for the PS solutions. It was seen that at high chain lengths (above ~300,000 g/mol) clusters in PS are found to be larger than those in PMMA, in agreement with observations for clusters formed in the respective homopolymer melts.\textsuperscript{86} However, in the limit of low chain length, clusters formed in PS solutions are smaller than those formed in solutions of PMMA with the equivalent polymer molecular weight. Determining the effect of polymer molecular weight on cluster size in the diblock copolymer case is somewhat more complex.
5.3 The effect of MMA block molecular weight on the size of metal clusters formed

As shown in Figure 5.3, neither the molecular weight of the styrene block, the overall chain molecular weight i.e. the sum of both styrene and MMA blocks or the wt% of MMA affect the cluster size in any consistent manner.

Figure 5.3 The effect of overall MW and PS MW (top) and MMA wt% (bottom) on cluster size.
Examining the diblock copolymers reveals that as the PMMA block MW increases, the cluster size decreases—regardless of the PS block MW or the solvent type. Moreover, the cluster sizes seem to correspond to those expected for the comparable homopolymer MW.

Figure 5.4: The effect of MMA block molecular weight on the size of metal clusters formed in PMMA homopolymer (full symbols) and copolymer (open symbols) suspensions, as listed in Table 5.1.

As shown in Figure 5.4, the effect of the MMA block MW on cluster size for those formed in the diblock copolymer media indeed follows the same trend as for clusters formed in PMMA homopolymer. Note that this trend holds regardless of the solvent type (common good, selective for PS or selective for PMMA).
In this phase of work, the effect of homopolymer and diblock copolymer molecular weight and composition on the synthesis of Co nanoclusters was examined. In all cases it was found that the clusters are relatively small (or order 70 nm or less), and their size distribution is relatively narrow.

It was found that in solutions of homopolymers in good solvent, the cluster size is minimal at a specific chain molecular weight, as shown in Figure 5.2: approximately 200,000 g/mol for PS, and 100,000 g/mol for PMMA. Clusters formed in low molecular weight PS are smaller than those formed in low molecular weight PMMA, but this trend reverses at higher chain molecular weight.

Two mechanisms have been suggested to explain the effect of polymeric media on cluster size and size distribution. The ‘polymer capping’ model \(^{86, 87}\) is based on the fact that polymer chains – whether in bulk or in solution – tend to adsorb onto the growing clusters, thus creating a layer that can inhibit growth. The capping model has been shown to successfully explain several system characteristics, such as the effect of chain molecular weight on cluster size in solution\(^ {87}\) and in bulk.\(^ {86}\) However, while the ‘polymer capping’ model successfully addresses the lack of clusters that are larger than the average size set by the capping mechanism, it cannot explain why smaller clusters are not found.

Recently, a study was conducted on the kinetics of cluster formation in bulk polymeric media.\(^ {86}\) It was shown that the narrow cluster size distribution can be attributed to a combination of cluster formation kinetics and the capping mechanism. The analysis shows that the average size of the clusters, \(R^*\), should scale as: \(^{97}\)
\[ R^* \sim \frac{\gamma}{\varepsilon} \] (1)

\( \gamma \) is the surface tension (energy per unit area) between the media and the cluster and \( \varepsilon \) is the energy of cluster formation per unit volume. \( \varepsilon \) defines the energy gain associated with metal atoms aggregating into a metal cluster when compared to their distribution in solution, and is thus relatively insensitive to the specific system. However, the surface tension is sensitive to the media properties: For clusters synthesized in a homogeneous solvent solution, \( \gamma \) is set by the chemical interactions between the cluster and the solvent. For clusters formed in bulk polymeric media, \( \gamma \) accounts not only for the chemistry of the system, but also for the effect of chain molecular weight.

In the case of cluster formation in a polymeric solution, the layer in contact with the cluster is composed of both solvent and polymer. Thus, the surface tension depends on the density of polymer in the adsorbed layer, \( \phi \):

\[ \gamma \sim (1-\phi)\gamma_s + \phi\gamma_p \] (2.a)

We have previously shown that \(^\text{12}\)

\[ \phi \sim \sqrt{\frac{\ln N}{N\left(1 - \sqrt{1 - \ln \frac{N}{N\delta^2}}\right)}} \] (2.b)

Here, \( \gamma_s \) is the interfacial tension between the solvent and the cluster, \( \gamma_p \) the surface tension between the polymer and the cluster, \( N \) is the degree of polymerization and \( \delta \) the adsorption energy gained by monomer adsorption onto the cluster surface, associated with the energy gain due to monomer-cluster interactions when compared to monomer-solvent. The resulting scaling for the optimal cluster size is then

\[ R^* \sim \frac{\gamma_s}{\varepsilon} + \frac{(\gamma_p - \gamma_s)}{\varepsilon} \sqrt{\frac{\ln N}{N\left(1 - \sqrt{1 - \ln \frac{N}{N\delta^2}}\right)}} \] (3)
Figure 5.5: The effect of homopolymer molecular weight on cluster size, as given by equation (3). $N$ and the cluster size are taken to be in arbitrary units.

In Figure 5.5 the cluster size as a function of chain molecular weight was plotted. It is seen that the cluster size is minimal at a finite chain length, as observed for both PS and PMMA suspensions.

The effect of di-block copolymer characteristics on the size of the Co clusters is more complex. In a common good solvent, where one might expect that the essential parameter setting the cluster size is the overall chain molecular weight, we find (Table 5.1) that clusters formed in a di-block copolymer with a combined molecular weight of 327,000 g/mol, are much smaller (20 nm) than those obtained in the similar molecular
weight PMMA homopolymer (31.5 nm), or the similar molecular weight PS homopolymer (42 nm) – both of them in their respective good solvents. The copolymer composition does not play a direct role in setting the cluster size either. Comparing copolymers with different overall molecular weights but similar MMA content (~50-60%) in similar solvents, yields different values for the average cluster sizes: 52 nm for a total molecular weight of 51,200 g/mol and 29 nm for a total MW of 266,900 g/mol. These may be explained by the different affinities of the two polymers to the cluster: After all, there is a difference in cluster size between those formed in PS of a given molecular weight and those in same molecular weight PMMA (Figure 5.2). However, we also find that the cluster size is nearly insensitive to the solvent type: Comparing clusters formed in the PMMA_{165800-b-PS_{101100}} in a solvent selective for the PS block (29 nm) are quite similar in size to those formed in the solvent selective for the PMMA block (32 nm). This observation is somewhat confusing, since in the former the solution of the di-block copolymer consists of micelles with a PMMA core and PS corona, while in the latter the micelles are reversed.

As shown in Figure 5.4, plotting the cluster size as a function of the PMMA block molecular weight yields an identical trend to that obtained for homopolymer PMMA – regardless of solvent quality and specificity. Thus, it must be concluded that the only parameter (for a fixed copolymer concentration) controlling the cluster size in suspensions of di-block copolymers is the molecular weight of one block, in this case PMMA, and is indifferent to other parameters including the molecular weight of the other block (PS) or the solvent quality.
Why PMMA and not PS? The interactions between PMMA and metal clusters are much stronger than those between the clusters and PS. \textsuperscript{86,97} Thus, the synthesis of Co nanoclusters in the PMMA-PS block copolymer suspension occurs within the MMA region exclusively, and is unaffected by the presence of the PS block. The solvent quality affects the cluster size to some degree (see Table 5.1), but only through its effect on the local PMMA concentration: In a common good solvent, the local concentration of the PMMA chains is set by the average solution concentration. In a selective solvent for the MMA, the local concentration is higher due to the formation of micelles with MMA coronas, whose concentration is higher than the average value. In a solvent selective for PS, the clusters form in the MMA core, namely, in a bulk MMA environment.
5.4 Summary

Synthesis of metal nanoclusters in polymeric media has been shown to yield small clusters with a narrow size distribution. Embedding such clusters in the three-dimensional structures formed by diblock copolymers will allow the development of ordered structures with high optical and magnetic contrast between the different regions. In this paper we investigate the effect of homopolymer and diblock copolymer properties on the cluster size. We find that in homopolymer solutions, the cluster size reaches a minimum at a finite chain MW. In the case of diblock copolymers, the cluster size is set by the block with the stringer affinity to the metal surface.
CHAPTER 6
POLYMER COMPOSITION AND SOLVENT EFFECTS ON THE
PHASE BEHAVIOR OF METAL NANOCLUSTER-BLOCK
COPOLYMER NANOCOMPOSITE

6.1 Overview
The design of self-assembled periodic organic/inorganic hybrid nanocomposites has drawn a great deal of attention in the past several years, especially due to their potential use in optoelectronic applications. These materials are characterized by the predictable phase separation of metal or metal oxide clusters within a polymer matrix according to a predetermined spatial architecture. There are various strategies to construct one-, two- and three-dimensional chemical patterns, most of which make use of “top down” fabrication techniques such as, for example, “soft” or dip pen nano-lithography. However, the most efficient approach is the use of the thermodynamically-driven phase separation and micro-domain formation in block copolymers, allowing a great deal of control over domain size and domain structure. Block copolymers are characterized by the incompatibility between different parts of the same polymeric chain and the formation of micro-domains. The structure of these micro-domains depends on the molecular weight of the blocks, their relative concentrations in the polymeric chain, the solvents used and the strength of their interactions with the blocks. In addition to their mesoscopic periodicity, block copolymers also possess favorable properties regarding their processibility, mechanical strength and thermal stability. Since the refractive index contrast between the microdomains in block copolymers is small, metal nanoparticles can be selectively
incorporated in order to augment the refractive index of one of the blocks \textsuperscript{136-137}. Upon transmission of light through such a nanocomposite, scattering intensity is substantially reduced when particle dimension is below 50-100nm. The spectral position, half width and the intensity of plasma resonance absorption in the visible and near infrared region were shown to depend on the particle size, shape, and the optical characteristics of both the polymer matrix and the nanocluster \textsuperscript{138}.

In order to produce useful nanocomposites, not only the size and shape of the particles will have to be controlled \textsuperscript{139-141}, but consideration must also be given to the location and distribution of the metal nanoparticles within the block copolymer matrix. Moreover, it has been shown that the final morphology and degree of periodicity of the block copolymer nanocomposite are not always as predicted from the expected thermodynamically-stable microstructure of the block copolymer template. Two main variables have a direct and crucial impact on this microstructure: (a) The relative concentration of the blocks in the block copolymer will determine various periodic microdomain structures consisting, for example, of spheres, cylinders or lamellae. The lamellae tend to form regularly repeating lamellar sequence, the cylinders arrange themselves in a bi-dimensional hexagonal lattice, while the spheres give rise to cubic lattices. (b) The nature of the solvent used in the system and its preferential affinity to one of the blocks. If the solubility of the two blocks in the solvent is not similar, the block copolymer will most likely behave as an amphiphilic molecule and generate micellar structures in solution. After the introduction of the metallic nanoparticles into the system and the removal of the solvent, the resulting microstructure may not coincide with the expected morphology based solely on block composition. Hence, this phenomenon may have an effect on the possible applications of that composite \textsuperscript{142-145}. By
changing the composition of the block copolymer, one can affect the morphology of the copolymer once it has self-assembled\textsuperscript{146-152}. The thermal conditions and solvent system used in synthesizing the nanocomposite also affect the final morphology obtained\textsuperscript{153-154}.

In this phase of work, we examine the effect of the solvent used in dissolving the block copolymer and the block copolymer relative composition on the ultimate morphology of the self-assembled nanocomposite. We examined two different cases, in an attempt to decouple the effects of the diblock composition and affinity to solvent on the morphology of the resulting nanocomposite: (a) Varying the block copolymer compositions while using a non-preferential solvent for either blocks, and (b) Using solvents that exhibit selectivity for one of the blocks, while keeping block copolymer composition constant. In this latter scenario, we looked at the effect of micelle formation in the reaction solution prior to metal nanoparticle introduction, and the effect of this process on the final overall morphology after the system underwent self-assembly and the solvent was removed.
6.2 Decomposition of $\text{Co}_2(\text{CO})_8$ in the $\text{PS}_{71,300}-\text{b-PMMA}_{11200}$ copolymer dissolved in cyclohexanone (a neutral solvent)

Figure 6.1 shows a TEM micrograph of the sample obtained from the decomposition of $\text{Co}_2(\text{CO})_8$ in the $\text{PS}_{71,300}-\text{b-PMMA}_{11200}$ copolymer that was dissolved in cyclohexanone. Based on the composition of this copolymer, which corresponds to a PS:PMMA ratio of about 6.3:1 (~13% PMMA), it is expected that the equilibrium microdomain structure formed upon self-assembly would consist of spheres of the shorter block, PMMA, formed in a matrix of the longer copolymer block, PS.

![Figure 6.1 Morphology of the cobalt-block copolymer nanocomposite formed by the decomposition reaction of $\text{Co}_2(\text{CO})_8$ in the $\text{PS}_{71,300}-\text{b-PMMA}_{11200}$ copolymer dissolved in cyclohexanone, which is an equally good solvent for both PS and PMMA. (a) Schematic of the expected morphology. (b) TEM micrograph of a sample of this system.](image)

Moreover, since the solvent is equally a good solvent for both the PS and the PMMA blocks, solvent effects will not be expected to play a role in altering the thermodynamically-predicted morphology. It has been previously shown that cobalt nanoparticles would be preferentially dispersed in the PMMA microdomain. Thus one
would expect to see cobalt-filled PMMA spheres dispersed in the PS matrix, as shown in the schematic image in Figure 6.1 (left). Indeed, this can be seen in the TEM micrograph, where there are fairly distinct darker spherical regions representing the cobalt-rich PMMA domains dispersed in lighter, cobalt-poor regions representing PS. The expected outcome is also supported by the fact that these cobalt regions are localized to certain areas of the micrograph, pointing to the dominance of PS as the matrix material.

6.3 Decomposition of $\text{Co}_2(\text{CO})_8$ in the $\text{PS}_{47,000}$-$b$-$\text{PMMA}_{280,000}$ copolymer dissolved in cyclohexanone

Figure 6.2 shows a TEM micrograph of the sample obtained from the decomposition of $\text{Co}_2(\text{CO})_8$ in the $\text{PS}_{47,000}$-$b$-$\text{PMMA}_{280,000}$ copolymer that was also dissolved in cyclohexanone. As in the previous sample, one would expect that the self-assembled structure formed when the solvent is removed to be spheres of the shorter block dispersed in a matrix of the longer block as well. In this case, however, the ratio of the blocks is reversed, i.e. PMMA is the larger block, with a PS:PMMA ratio of 1:6.1 (~86% PMMA). Hence, in this case, the microdomain structure corresponds to PS spheres in a PMMA matrix. Since, as described previously, the solvent is equally a good solvent for both the PS and the PMMA blocks, solvent effects on morphology are negligible in this case as well.
Figure 6.2. Morphology of the cobalt-block copolymer nanocomposite formed by the decomposition reaction of Co$_2$(CO)$_8$ in the PS$_{47,000}$-b-PMMA$_{280,000}$ copolymer dissolved in cyclohexanone, which is an equally good solvent for both PS and PMMA. (a) Schematic of the expected morphology. (b) TEM micrograph of a sample of this system.

The schematics of the expected nanocomposite morphology shown in Figure 6.2 (left) is supported by the TEM micrograph, in which there is an almost homogeneous distribution of the cobalt nanoparticles surrounding regularly spaced lighter regions. In this system, the lighter regions are the PS spheres and the cobalt particles are dispersed mainly in the predominant PMMA matrix.

6.4 Decomposition of Co$_2$(CO)$_8$ in PS$_{101,100}$-b-PMMA$_{165,800}$ dissolved in 2-ethoxyethanol (a preferential solvent for PMMA)

The micrograph shown in Figure 6.3 is that of a nanocomposite sample created by the decomposition of Co$_2$(CO)$_8$ in PS$_{101,100}$-b-PMMA$_{165,800}$ (composition consisting of ~64% PMMA) dissolved in 2-ethoxyethanol. This particular experiment was an attempt to investigate the effect of the quality of the solvent on the final morphology of the nanocomposite. 2-ethoxy ethanol is a good solvent for PMMA, and a non-solvent for PS$^{156}$. 

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Figure 6.3 Morphology of the cobalt-block copolymer nanocomposite formed by the decomposition reaction of Co$_2$(CO)$_8$ in PS$_{101,100}$-b-PMMA$_{165,800}$ dissolved in 2-ethoxy ethanol, which is a preferential solvent for PMMA. (a) Schematic of the expected morphology. (b) TEM micrograph of a sample of this system (negative).

As a result of the preferential affinity of the solvent to the PMMA block, the solution will contain micelles consisting of a PS core surrounded by a PMMA shell, as shown in the schematics of Figure 6.3 (left). The TEM micrograph does indeed show distinct micellar structures, with cobalt particles distributed on the corona of the micelles, but absent from the core. This is precisely the expected morphology, since the corona consists of PMMA and the cobalt nanoparticles are preferentially attracted to the PMMA block. Thus, the final self-assembled morphology retains the morphology obtained in solution before the synthesis was started, and not the thermodynamically-expected morphology, which, for this particular block copolymer composition, should be a metastable bicontinuous microstructure. Since the TEM samples were created by the fast evaporation of the solvent from the droplet placed on the grid, the block copolymer remained kinetically trapped in its solution micellar structure, without the possibility of undergoing a phase transformation to its equilibrium morphology.
6.5 Decomposition of Co$_2$(CO)$_8$ in PS$_{101,100}$-b-PMMA$_{165,800}$ dissolved in toluene (a preferential solvent for PS)

The micrograph shown in Figure 6.4 is that of a nanocomposite sample created by the decomposition of Co$_2$(CO)$_8$ in PS$_{101,100}$-b-PMMA$_{165,800}$ (composition consisting of ~64% PMMA) dissolved in toluene, is a good solvent for PS, and a non-solvent for PMMA$^{157}$. As a result of the preferential affinity of the solvent to the PS block, the solution will contain micelles consisting of a PMMA core surrounded by a PS shell, as shown in the schematics of Figure 6.4 (left).

Figure 6.4. Morphology of the cobalt-block copolymer nanocomposite formed by the decomposition reaction of Co$_2$(CO)$_8$ in PS$_{101,100}$-b-PMMA$_{165,800}$ dissolved in toluene, which is a preferential solvent for PS. (a) Schematic of the expected morphology. (b) TEM micrograph of a sample of this system.

The TEM micrograph shows cobalt aggregates that are randomly distributed in a polymer matrix. This is precisely the expected morphology, since the core of the micelles consists of PMMA and the cobalt nanoparticles are preferentially attracted to the PMMA block. Thus, in this case as well, the final self-assembled morphology retains the morphology obtained in solution before the synthesis was started, and not the
thermodynamically-expected morphology, which, for this particular block copolymer composition, should be a metastable bicontinuous microstructure.

Figure 6.5 The top two TEM micrographs show a homogeneous dispersion of cobalt particles in the matrices of PS (6.5a) and PMMA (6.5b) homopolymers. Figures 6.5c and 6.5d show the phase transformation that occurred upon annealing of the samples shown in Figures 6.3 and 6.4.

A better appreciation for the influence of the solvent on the pattern of particle dispersion may be drawn by examining the images in Figure 6.5. The top two TEM micrographs show a homogeneous dispersion of cobalt particles in the matrices of PS (6.5a) and PMMA (6.5b) homopolymers. The actual particle morphology and average size is strongly influenced by the nature of their interfacial interactions with the polymer$^{158-159}$, but their spatial distribution in the respective matrices is independent of
the polymer itself. It is quite evident that the distribution of the cobalt particles in the homopolymer matrices differs considerably from their distribution in the block copolymer matrices. When samples of cobalt-containing homopolymer matrices are further annealed just above their glass temperatures, there is no noticeable change in the particle morphology and distribution. We have shown that in the melt, particle size is determined almost exclusively by the strength of interactions between the polymer matrix and the particles\textsuperscript{159}, and hence, in this case, these interactions would have already occurred during particle formation, and therefore, no further changes are expected. Similar results were also obtained for block copolymer composite samples in which the template morphology was determined by the copolymer composition. In these cases (Figures 6.1 and 6.2), the specific microstructure that was formed upon the removal of the non-preferential solvent remained intact even after annealing. However, when the same thermal treatment was applied to the block copolymer composites that were created in preferential solvents (Figures 6.3 and 6.4), additional changes in the distribution patterns were observed. Since in these cases the dissolved block copolymer remained kinetically trapped in the micellar structure in which it has organized itself in solution, the annealing process allowed the additional rearrangement of the chains to the thermodynamically-stable microstructure dictated by the block composition. Figures 6.5c and 6.5d show the phase transformation that occurred upon annealing of the samples shown in Figures 6.3 and 6.4, respectively. Interestingly, the block copolymer micelles having metal nanoparticles embedded in their shell domain (as shown in Figure 6.3), underwent the most dramatic phase transformation, while the morphology of the block copolymer having metal nanoparticles embedded in their core domain of the micelles (as shown in Figure 6.4) underwent only a limited phase transformation.
The spatial distribution of the cobalt nanoparticles synthesized in these experiments coincides with the morphology dictated by thermodynamically-driven microdomain structure of the block copolymer, provided the solvent used is an equally good for both blocks of the copolymer. If a solvent with selective affinity is used, the overall final morphology of the nanocomposite is “locked” into place while in solution, and the evaporation of the solvent, whether fast or slow, or the annealing of the solid samples does not cause this morphology to change.
6.6 Summary

In this work we examined the effect of the solvent used in dissolving a block copolymer and the block copolymer relative composition on the ultimate morphology of a self-assembled metal cluster-block copolymer nanocomposite. We studied two different cases, in an attempt to decouple the effects of the diblock composition and affinity to solvent on the morphology of the resulting nanocomposite: (a) Variation of the block copolymer compositions while using a non-preferential solvent for either blocks, and (b) Variation of preferential solvents while keeping block copolymer composition constant. In this latter scenario, we looked at the effect of micelle formation in the reaction solution prior to metal nanoparticle introduction, and the effect of this process on the final overall morphology after the system underwent self-assembly and the preferential solvent was removed. We found that the spatial distribution of the metal clusters synthesized in-situ coincided with the morphology dictated by thermodynamically-driven microdomain structure of the block copolymer. Moreover, the overall final morphology of the nanocomposite is “locked” into place while in solution, and fast solvent evaporation does not cause this morphology to change.
CHAPTER 7

EFFECT OF METAL PRECURSOR CONCENTRATION ON THE KINETICS OF NANOCOMPOSITE SYNTHESIS

As mentioned before, FTIR is a powerful analytical tool in measuring the rate of chemical reactions. The decomposition of cobalt carbonyl into cobalt nanoclusters was studied in polystyrene and polymethylmethacrylate. The PS had a MW of 100,000, and the PMMA had a MW of 120,000. The analysis was done while keeping the weight percent of polymer constant and changing the initial concentration of metal precursor. In this way, a correlation between the rate of reaction and initial carbonyl concentration could be made. A comparison between the rate of decomposition in PS versus PMMA was also possible. This result could be used to explore the nature of interaction of the interaction between the cobalt nanoclusters and the polymer chains, since the rate of decomposition would be affected by the type or lack of bonding between the growing clusters and the polymer matrix. Combined with the rest of the results in this study, the data obtained in the kinetic work could shed more light on the strength of interaction between the different components of the nanocomposite. By analyzing the spectra, looking specifically for the presence of new peaks, this technique could be used to examine the possible formation of chemical bonds between the cobalt clusters and the polymer that they are dispersed in. As mentioned earlier, the decomposition of cobalt carbonyl occurs in two steps. It is the second reaction, or decomposition of \( \text{Co}_4(\text{CO})_{12} \), that will be monitored more closely in this study to compute the rate of the decomposition reaction.
Figure 7.1 Decomposition of Co$_2$(CO)$_8$ in a PS matrix with a MW of 100,000 g/mol

The initial undecomposed sample shows a peak at around 1870 cm$^{-1}$ and another shoulder around 1885 cm$^{-1}$. The peak at 1870 cm$^{-1}$ would correspond to the Co$_2$(CO)$_8$ species while that at 1885 cm$^{-1}$ would correspond to the Co$_4$(CO)$_{12}$ species. They are shifted from the expected values of 1858 cm$^{-1}$ and 1867 cm$^{-1}$ possibly because of solvent effects. The initial sample shows some Co$_2$(CO)$_8$, but the subsequent peaks show the decomposition of the Co$_4$(CO)$_{12}$ species.
The decomposition of the Co₄(CO)₁₂ band was calculated using the following IR equation:

\[ A = \epsilon \cdot d \cdot c \]  \hspace{1cm} (1)

Where A is the peak height or absorbance, \( \epsilon \) is the molar absorption extinction coefficient, d is the spacer width of the FTIR cell, and c is the concentration of the Co₄(CO)₁₂. The first step was calculating the molar absorption extinction coefficient using the previous equation (1).

\[ \epsilon = \frac{A}{d \cdot c} \]  \hspace{1cm} (2)

In order to calculate \( \epsilon \), the initial undecomposed spectrum was used, with 5 x 10⁻³ M as the concentration and 0.012cm as the spacer width. A graph was plotted of A vs dc for each concentration and the slope of this graph, which was equal to \( \epsilon \), was found. This value of the extinction coefficient which is a constant for the particular system, was then used to calculate the concentration of Co₄(CO)₁₂ at each time reading.
Once the concentration of the Co₄(CO)₁₂ was calculated at each time sampling, the order of the reaction was determined. The following equation could be used to equate time versus concentration of the reaction:

\[ \frac{dc}{dt} = -kc \]  \hspace{1cm} (3)

where \( c \) is the concentration in mol/L, \( t \) is the time in seconds, and \( k \) is the reaction rate. By separating the variables and integrating both sides of the equation, the following relationship is obtained:

\[ \ln(c_o) - \ln(c) = kt \]  \hspace{1cm} (4)

where \( c_o \) is the initial concentration. A plot of \( \ln(c) \) vs time would yield the reaction rate \( k \) as the slope. The following plot shows the data obtained for the decomposition of 5 \( \times 10^{-3} \) M Co₂(CO)₈ in 100,000 g/mol PS:
As seen in the graph, the first trend shows an increase in the concentration up to 30 minutes followed by the subsequent decrease in the value of concentration. In previous work this was found to be possibly due to the fact that the polymer provides a solid support for the nucleation of the growing nanoclusters. This is similar to the nucleation process in homogeneous nucleation in which the polymer chains can act as sites for nucleation, and hence cause an initial increase in the rate of nanocluster formation. The plot shows a linear relationship which means that the reaction is a first order reaction. The slope of the graph shows that the reaction rate $k$ is $8 \times 10^{-5}$ s$^{-1}$. The spectrum showing the decomposition of of $15 \times 10^{-3}$ M $\text{Co}_2(\text{CO})_8$ in 100,000 g/mol PS is seen on the following page.

**Figure 7.2** Plot of $\ln (c)$ vs. time for the decomposition of $5 \times 10^{-3}$ M $\text{Co}_2(\text{CO})_8$ in 100,000 g/mol PS
Figure 7.3 Decomposition of $15 \times 10^{-3}$ M $\text{Co}_2(\text{CO})_8$ in 100,000 g/mol PS matrix.

In this case, the general trends are the same, except the decomposition did not begin as early as the previous example. The concentration peaked at 60 minutes, followed by the subsequent decrease in concentration. The absorbance levels are also higher as compared to the previous case possibly due to the fact that a higher initial concentration of metal precursor was used. The initial undecomposed peak also shows the presence of some $\text{Co}_2(\text{CO})_8$ in addition to $\text{Co}_4(\text{CO})_{12}$. Using this data, the resulting plot of $\ln(c)$ vs time is shown on the following page:
The rate of this reaction can be taken from the slope of the ln(c) vs time graph as mentioned before. In this case the reaction rate is found to be $1 \times 10^{-4}$ s$^{-1}$. The graph is also linear meaning that this reaction is first order except for the initial section. It can be seen that there was an increase in the reaction rate as the concentration of the cobalt precursor increased. The FTIR plot showing the decomposition of Co$_2$(CO)$_8$ with an initial concentration of $20 \times 10^{-3}$ M in the PS matrix is shown on the next page:
Figure 7.5 Decomposition of $2 \times 10^{-3}$ M $\text{Co}_2(\text{CO})_8$ in 100,000 g/mol PS matrix.

As seen with the previous plots, the initial increase in concentration is seen, before a sequential decrease as time increases. This plot also shows that it took even longer before the $\text{Co}_4(\text{CO})_{12}$ decomposition or the second step took place. In this case it started after 105 minutes, and this is possibly due to the fact that at a higher concentration, there was more initial $\text{Co}_2(\text{CO})_8$ to convert before the actual decomposition could take place. The corresponding $\ln(c)$ vs time graph for this reaction can be seen on the following page.
Figure 7.6 Plot of \( \ln(c) \) vs. time for the decomposition of \( 20 \times 10^{-3} \text{ M Co}_2(\text{CO})_8 \) in \( 100,000 \text{ g/mol PS} \)

The rate of this reaction, as taken from the slope of the curve, is \( 2 \times 10^{-4} \text{ s}^{-1} \). This value is double the rate of the previous concentration of \( 15 \times 10^{-3} \text{ M Co}_2(\text{CO})_8 \). As in the previous cases, the graph remains linear meaning that the reaction is a first order reaction. By taking all the results together, one can begin to understand the influence of precursor concentration on the decomposition reaction rate. This can be used in tailoring future reactions based on this metal nanoparticle-polymer system. A table showing the reaction rates and initial \( \text{Co}_2(\text{CO})_8 \) concentration can be seen on the other page:
Table 7.1 Comparison of rate constant and Co$_2$(CO)$_8$ concentration during decomposition in 100,000 g/mol PS

<table>
<thead>
<tr>
<th>Co$_2$(CO)$_8$ Concentration</th>
<th>k (s$^{-1}$)</th>
<th>$\varepsilon$ (L/mol*cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 x 10$^{-3}$ M</td>
<td>8 x 10$^{-5}$</td>
<td>1951.7</td>
</tr>
<tr>
<td>15 x 10$^{-3}$ M</td>
<td>1 x 10$^{-4}$</td>
<td>1951.7</td>
</tr>
<tr>
<td>20 x 10$^{-3}$ M</td>
<td>2 x 10$^{-4}$</td>
<td>1951.7</td>
</tr>
</tbody>
</table>

Comparing all of the data from these reactions shows that the reaction rate of the decomposition in the PS matrix increases as the concentration of cobalt precursor increases. In order to understand the differences in interaction between the cobalt nanoparticles and the different blocks in the PS-b-PMMA copolymer, the same type of kinetic analysis was carried out using the PMMA homopolymer also. A comparison of the data between the two different polymeric systems, will further the understanding of the interfacial interactions from a kinetic standpoint. The FTIR spectrum of the decomposition of 5 x 10$^{-3}$ M Co$_2$(CO)$_8$ in 120,000 g/mol PMMA matrix is shown on the next page:
As seen with the PS samples, the initial undecomposed sample shows a peak at around 1870 cm\(^{-1}\) and another shoulder around 1885 cm\(^{-1}\). The peak at 1870 cm\(^{-1}\) would correspond to the Co\(_2\)(CO)\(_8\) species while that at 1885 cm\(^{-1}\) would correspond to the Co\(_4\)(CO)\(_{12}\) species. They are shifted from the expected values of 1858 cm\(^{-1}\) and 1867 cm\(^{-1}\) possibly because of solvent effects. The initial sample shows some Co\(_2\)(CO)\(_8\), but the subsequent peaks show the decomposition of the Co\(_4\)(CO)\(_{12}\) species starting after 30 minutes. Similar to the PS samples, the concentration at each time reference was calculated using equations 1-4 and a graph of ln (c) vs time for the decomposition reaction is presented on the following page.
Figure 7.8 Plot of ln (c) vs. time for the decomposition of 5 x10^{-3} M Co_2(CO)_8 in 120,000 g/mol PMMA

This plot is again similar to the previous ones showing an initial increase in concentration followed by a linear decrease. As was mentioned before, the increase is possibly due to the fact that the polymer provides a solid support for the nucleation of the growing nanoclusters. This behavior is similar to the nucleation process in homogeneous nucleation in which the polymer chains can act as sites for nucleation, and causes an initial increase in the rate of nanocluster formation. The linear nature of the curve means that the reaction in PMMA is also first order. The slope of the curve, which is the reaction rate constant, has a value of 6 x 10^{-5} s^{-1}.
The concentration of the $\text{Co}_2(\text{CO})_8$ was increased to $15 \times 10^{-3}$ M and the decomposition was then carried out under the same conditions as the previous experiment. The following is the FTIR spectra obtained in that reaction:

![Figure 7.9 Decomposition of $15 \times 10^{-3}$ M $\text{Co}_2(\text{CO})_8$ in 120,000 g/mol PMMA](image)

In this experiment, the general trend is the same as the first decomposition in PMMA, including the fact that the decomposition of the $\text{Co}_4(\text{CO})_{12}$ began at the same point as the previous example. The concentration peaked at 30 minutes, followed by the subsequent decrease in concentration. Here, the absorbance levels are also higher as compared to the previous case possibly due to the fact that a higher initial concentration of metal precursor was used. The initial undecomposed peak also shows the presence of some $\text{Co}_2(\text{CO})_8$ in addition to $\text{Co}_4(\text{CO})_{12}$. 

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Using the data obtained from the FTIR spectra, the resulting plot of $\ln(c)$ vs time is shown below:

![Plot of $\ln(c)$ vs. time for the decomposition of 15 x $10^{-3}$ M Co$_2$(CO)$_8$ in 120,000 g/mol PMMA](image)

**Figure 7.10** Plot of $\ln(c)$ vs. time for the decomposition of 15 x $10^{-3}$ M Co$_2$(CO)$_8$ in 120,000 g/mol PMMA

The rate of this reaction can be taken from the slope of the $\ln(c)$ vs time graph as mentioned before. In this case the reaction rate is found to be $8 \times 10^{-5}$ s$^{-1}$. This represents an increase in the rate over the previous experiment in which a lower initial concentration of metal precursor was used. The graph is also linear meaning that this reaction is first order except for the initial section. The FTIR plot showing the decomposition of Co$_2$(CO)$_8$ with an initial concentration of 20 x $10^{-3}$ M in the PMMA matrix is shown on the next page:
This spectrum is similar to the others in which there is an initial increase in concentration, before a sequential decrease as time increases. The one difference is that it took a longer time for the Co$_4$(CO)$_{12}$ decomposition or the second step in the decomposition to take place. In this case it started after 105 minutes, and this is possibly due to the fact that at a higher concentration, there was more initial Co$_2$(CO)$_8$ to convert before the actual decomposition could take place. It is interesting to note that in the case of PS with the same Co$_2$(CO)$_8$ concentration, the onset of the Co$_4$(CO)$_{12}$ decomposition occurred after the same time. The corresponding ln(c) vs time graph for this reaction can be seen on the following page.
As taken from the slope of the curve, the rate of this reaction is found to be $8 \times 10^{-5}$ s$^{-1}$. This shows that there was no appreciable change in reaction rate when the concentration of the precursor was increased from $15 \times 10^{-3}$ M to $20 \times 10^{-3}$ M. The graph is also linear meaning that this reaction is also first order. The following table shows the comparison between reaction rate and initial Co$_2$(CO)$_8$ concentration for the decomposition reaction in the PMMA matrix:

**Table 7.2** Comparison of rate constant and Co$_2$(CO)$_8$ concentration during decomposition in 120,000 g/mol PMMA

<table>
<thead>
<tr>
<th>Co$_2$(CO)$_8$ Concentration</th>
<th>k (s$^{-1}$)</th>
<th>$\varepsilon$ (L/mol*cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-3}$ M</td>
<td>$6 \times 10^{-3}$</td>
<td>6669</td>
</tr>
<tr>
<td>$15 \times 10^{-3}$ M</td>
<td>$8 \times 10^{-5}$</td>
<td>6669</td>
</tr>
<tr>
<td>$20 \times 10^{-3}$ M</td>
<td>$8 \times 10^{-5}$</td>
<td>6669</td>
</tr>
</tbody>
</table>
In addition to comparing the rates of reactions as concentration increases in each particular homopolymer, it is also interesting and more informative to compare the rates of reactions at the same concentration between the two homopolymer solutions. Table 7.3 is a comparison of the reaction rates between polymer types.

Table 7.3 Comparison of reaction rates of the decomposition of Co$_2$(CO)$_8$ in the PS and PMMA homopolymer matrices at the same initial concentration.

<table>
<thead>
<tr>
<th>Co$_2$(CO)$_8$ Concentration</th>
<th>k (s$^{-1}$) in PS</th>
<th>k (s$^{-1}$) in PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 x10$^{-3}$ M</td>
<td>8 x 10$^{-5}$</td>
<td>6 x 10$^{-5}$</td>
</tr>
<tr>
<td>15 x10$^{-3}$ M</td>
<td>1 x 10$^{-4}$</td>
<td>8 x 10$^{-5}$</td>
</tr>
<tr>
<td>20 x10$^{-3}$ M</td>
<td>2 x 10$^{-4}$</td>
<td>8 x 10$^{-5}$</td>
</tr>
</tbody>
</table>

Comparing the two polymeric systems, it was seen that the decomposition reaction rate was faster in the PS system as compared to the PMMA system. This was due to the fact that the decomposition of the carbonyl in the PMMA led to a chemical bond that made the release of CO more difficult. So although the PMMA provided more sites for nucleation during the decomposition, the actual growth of the nanoparticles occurred faster in the PS matrix.
CHAPTER 8

CONCLUSIONS

This work looked at the selective interfacial interactions between cobalt nanoparticles and diblock copolymers using different approaches that probed the metal nanoparticle surface interactions with both the diblock copolymer itself and its constituent homopolymer blocks. The results from this work will enable researchers to synthesize these metal nanoparticles in a deliberate and structured way because the data will begin to elucidate ways in which the metal nanocluster nucleation and growth mechanism could be controlled. It will also help to shed some light on the control of the interfacial interactions between polymers and metal nanoparticles. This is important because it is these interactions that govern the formation, stabilization and spatial distribution of metal nanoparticles within a block copolymer matrix. The results of this work will also illuminate the role of the difference in reactivity between the copolymer blocks, as it pertains to nanocomposite synthesis.

As was mentioned earlier, different approaches were taken to probe the nanocluster-polymer interaction, and in the first approach, the effect of system properties and adsorption sequence on competitive adsorption of poly(methyl-methacrylate) (PMMA) and polystyrene (PS) on narrowly polydisperse cobalt (Co) nanoparticles (D ~ 27 nm) was investigated. One of the first results seen was that regardless of the polymer suspension properties, the particle size is similar, of order 15-20 nm in radius, and the size distribution as given by the range of sizes is relatively narrow. Subsequent
processing (e.g. immersion in another polymeric solution) did not affect the resulting particle size.

TGA was the main technique use to probe the surface interaction, and it was found to be an effective way of analyzing the surface interactions between different polymers and the surfaces of the metal nanoparticles, since the it has been shown that the thermal degradation of adsorbed polymers is directly related to the strength of interaction between the polymer chains and the substrate. Using TGA analysis, it was found that in PS films, the main scission temperature decreases consistently with decreasing film thickness while in PMMA films the film thickness does not significantly affect the main-chain scission transition. It was found though that adsorption of PMMA onto Co nanoparticles suppresses the side-chain transition due to stabilization of the side – chains against scission arising from the coordination of the carbonyl groups on the acrylate side group with the reactive cobalt surface sites.

It was also found that in the case of adsorption of the homopolymers on to the cobalt nanoparticles, the order of adsorption (PS and then PMMA, PMMA and then PS, or adsorption from a mixture) did not affect the composition of the adsorbed layer in systems where the mixed solvent is good for both polymers (namely, the chlorobenzene content is lower than ~50%). In these cases, it was found that the adsorbed layer is dominated by PMMA (the more reactive polymer), evidenced by the fact that all of the TGA traces for these different systems resembled that of Co-PMMA system.

While PMMA was found to adsorb more strongly in common good solvents, the result showed that the level of adsorption of PMMA depended on the solvent quality. In comparing the TGA profile of the adsorbed polymer layer in a solvent that was good for both polymers (1:6 chlorobenzene to toluene) to that obtained in a selective solvent that is
poor for PS (2:1 chlorobenzene to toluene), it was seen that the composition of the adsorbed layer differs significantly. In the common good solvent PMMA displaced the adsorbed PS completely, but this was not the case in the selective solvent. It was found that the TGA profile of the adsorbed layer in the latter case could be approximated by a linear superposition of the Co-PS and PMMA film profiles. This showed that the adsorbed film contained 55% PS, and 45% PMMA. This fact proved interesting because it is expected that in the poor solvent, PS should form a dense layer on the particles that would inhibit adsorption of PMMA. This would be due to the fact that the polymer-substrate interaction should be stronger than the polymer-solvent in a poor solvent. The presence of an appreciable amount of PMMA on the surface, in addition to PS, indicated that the PS did not saturate all surface sites, i.e. a large fraction of them remains available. This agreed with previous results like the ones obtained from TEM, in which lack of complete stabilization by PS led to the formation of chainlike structures since more sites were available for cobalt nanoclusters to aggregate. Thus adsorption of polymers on metal nanoparticles depends both on the strength of the polymer-substrate interaction and the solvent quality: a strongly-interacting polymer will displace a weakly-interacting one only if the solvent is a good (or moderate) solvent for the weakly interacting polymer. In a poor solvent, weakly interacting polymers cannot be displaced, but due to the availability of ‘free’ surface sites co-adsorption is possible, thus leading to the formation of a mixed adsorbed layer, which is different to what is observed in the bulk case.

In the second approach, the effect of homopolymer and diblock copolymer properties on the metal nano-cluster size was investigated. Looking at the homopolymers separately, it was found that in both types of homopolymer suspensions, the cluster size is
minimal at a finite chain molecular weight. For the PMMA suspensions, the chain molecular weight was approximately 200,000 g/mol, and for the PS suspensions it was 100,000 g/mol. The results showed that at high chain lengths (above ~300,000 g/mol) clusters in PS are found to be larger than those in PMMA, in agreement with observations for clusters formed in the respective homopolymer melts. However, it was found that in the limit of low chain length, clusters formed in PS solutions are smaller than those formed in solutions of PMMA with the equivalent polymer molecular weight.

When analyzing the effect of di-block copolymer characteristics on the size of the Co clusters, it was found that the copolymer composition, including overall chain molecular weight, does not play a direct role in setting the cluster size. Also, it was seen that the cluster size is nearly insensitive to the solvent type. Analysis of the results showed that the only parameter (for a fixed copolymer concentration) controlling the cluster size in suspensions of di-block copolymers is the molecular weight of one block, in this case PMMA, and is indifferent to other parameters including the molecular weight of the other block or the solvent quality.

The effect of polymer composition and solvent choice on the morphology of the nanocomposite was also investigated. It was found that when a neutral solvent was used, the spatial distribution of the cobalt nanoparticles synthesized in these experiments coincided with the morphology dictated by thermodynamically-driven microdomain structure of the block copolymer.

The results also showed that if a solvent with selective affinity is used, the overall final morphology of the nanocomposite is “locked” into place while in solution, and the evaporation of the solvent, whether fast or slow, or the annealing of the solid samples did
not cause this morphology to change. In this case micelles were formed with the cobalt residing in the micelle region made up of the more reactive polymer block (PMMA).

Finally, the kinetics of the decomposition reaction in the homopolymer suspension was studied. The reactions were carried out using successively higher initial concentrations of metal precursor. It was found that as the concentration of the cobalt carbonyl increased, the rate of the reaction increased in each homopolymer. In PS_{100,000}, the initial carbonyl concentrations were 5 \times 10^{-3} \text{M}, 15 \times 10^{-3} \text{M} and 20 \times 10^{-3} \text{M}. The resulting rates were 8 \times 10^{-5} \text{s}^{-1}, 1 \times 10^{-4} \text{s}^{-1} and 2 \times 10^{-4} \text{s}^{-1} respectively. In PMMA_{120,000}, the reaction rates were 6 \times 10^{-5} \text{s}^{-1}, 8 \times 10^{-5} \text{s}^{-1} and 8 \times 10^{-5} \text{s}^{-1} respectively for the same concentrations used in the PS experiments. Comparing the two polymeric systems, it was seen that the decomposition reaction rate was faster in the PS system as compared to the PMMA system.

This was due to the fact that the decomposition of the carbonyl in the PMMA led to a chemical bond that made the release of CO more difficult. So although the PMMA was providing more sites for nucleation during the decomposition, the actual growth of the nanoparticles occurred faster in the PS matrix.
CHAPTER 9
RECOMMENDATIONS

The techniques used in this study provided a semi-quantitative measure of the strength of interaction between the cobalt nanoparticles and the functional groups present on the poloymer chains. Techniques in which a fully quantitative method could be used, should be explored. This would allow researchers to build a series of reactivities among functional groups to the cobalt nanocluster surface. Research already done has shown that atomic force microscopy (AFM) can be used to measure the actual force of interaction between a substrate and a another species deposited on its surface. Therefore, one way to provide a quantitative measure is to AFM on a model surface, on which cobalt nanoclusters have been deposited.

One possible way to do this is by creating a self-assembled monolayer (SAM) of thiol molecules on a gold surface. One end of the molecule will contain the thiol functionality while the other side will have the functional group of interest. The thiol will bond to the gold surface, leaving the other functional group end exposed to air. Cobalt or other metal particles can then be deposited onto the surface by decomposing the metal precursor in the gaseous phase, and the strength of interaction between the metal nanoclusters and the functionalized surface can be probed with AFM. AFM can also be used to provide information about the clustering on the surface, which will indicate the type of interactions between the metal nanoparticles and the functional groups on the surface. For good interaction, the particles will spread along the surface. Any type of morphological characterization of this surface should give a relatively flat surface. For weaker interactions, the particles will tend to cluster rather than spread. Imaging this surface should result in a rough surface showing distinct cluster formation.
As mentioned before, using this particular *in-situ* method for synthesizing the nanocomposites has many advantages over the other techniques. The one aspect of the synthesis that needs more study is the final morphology of the nanocomposite films. Although the morphologies obtained were similar to the ones obtained using other techniques, they were not as well defined. This may be possibly due to other interactions between the different components while in solution. Therefore, in order to obtain the desired morphology in a consistent manner, the reasons for these inconsistencies, as well as methods for producing the exact morphologies should be studied. This may include changing the processing methods by adding an annealing stage, or studying the rate of solvent evaporation from the film to optimize the resulting morphology.

During the test of competitive adsorption, one strongly interacting and one weakly interacting polymer were used. In order to fully understand the influence of polymer reactivity on the formation and stabilization of nanoclusters, other polymer pairs should be tested. Homopolymer pairs in which both are strongly interacting, or the opposite of this situation in which both are weakly interacting, should be tested. This may provide deeper understanding of other types of polymer-cluster interactions.

This study focused on the PS-b-PMMA diblock copolymer system. For future work, other copolymer systems should be tested. Copolymers that are used in microelectronics and that are readily commercially available should be included. Also different type of copolymer systems, for example amphiphilic block copolymers or biocompatible copolymer, should be examined because researchers will have access to the different environments and functionalities that these polymers can provide.
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