NANOMETER-SCALE METAL DISPERSIONS IN POLYMERIC MATRICES

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ABSTRACT

We have investigated the diffusive properties of model metal nanoparticle dispersions in polymeric matrices of several different molecular weights. Rutherford Backscattering Spectrometry was used to measure the depth distribution of gold nanoparticles within thin layers of poly(t-butyl acrylate) (PTBA). The gold nanoparticles were created by evaporation of a discontinuous gold layer onto a thin film of PTBA. A second PTBA film was placed onto these samples to create "sandwiches" in which the gold existed between two PTBA films. Gold particle diffusion coefficients were obtained from measured gold particle depth distributions in annealed samples for which the molecular weights of the two PTBA layers were identical. The experiments revealed that particle mobility was decreased by two to three orders of magnitude compared with the predictions of the Stokes-Einstein model of particle diffusion. These results are attributed to bridging interactions between particles arising from slow exchange kinetics of polymer segments at the polymer/metal interface. Experiments for which the molecular weights of the two polymer films are different are sensitive to the ability of polymer molecules to pass through the gold particle layer. Experiments done with thermally evaporated particles are consistent with a picture in which polymer molecules are able to freely pass through the gold particle layer. Results obtained with gold deposited by electron-beam evaporation are strikingly different. The gold in this case is not able to diffuse, and polymer molecules are not able to penetrate the gold layer. These results, in addition to preliminary results from optical absorption experiments, indicate that much smaller particles are obtained by electron-beam evaporation than by thermal evaporation.

INTRODUCTION

Metal particle dispersions have a variety of interesting optical, magnetic and electronic properties which enable them to be utilized in a variety of technologies. Many of these properties require that the particles be dispersed in an electrically insulating, optically transparent medium, such as a polymer. Appropriate choice of the polymer allows one to control the morphology of the metal particle dispersion, and hence control the properties of interest. Several groups have used the self-organizing ability of block copolymers, for example, in an attempt to control both the size and spatial distribution of nanometer-scale metal particles.\textsuperscript{1-5} The idea in this case is to use a highly organized block copolymer microstructure, with characteristic domain sizes of tens of nanometers, as "templates" for controlling the distribution of the metal particles. Block copolymer systems are chosen so that the metal particles preferentially segregate to one type of polymer domain. If one particle exists in each domain, and the block copolymer morphology is maintained during the incorporation of the metal particles, then one should have excellent morphological control over the metal particle dispersion. A significant complication arises, however, in that there is almost always more than one metal particle in an individual domain, even
for domains as small as 10 nm. Coalescence of these metal particles is generally very slow, and one therefore loses control of the size of the metal particles. In this example, one must first understand how particles are able to diffuse and coalesce within a single domain of uniform composition. These processes can be more readily understood by studying the properties of metal particle dispersions in homopolymers of different compositions. These simpler types of dispersions are the subject of the work described here.

Previously, it was shown that gold nanoparticles, produced either by thermal evaporation or by reduction of HAuCl₄, behave very differently in polymer matrices that in many ways are quite similar.⁶,⁷ Consider, for example, the three polymer structures shown in figure 1:

![Chemical structures of polystyrene (PS), poly(2-vinylpyridine) (PVP) and poly(t-butyl acrylate) (PTBA).](image)

**Figure 1:** Chemical structures of polystyrene (PS), poly(2-vinylpyridine) (PVP) and poly(t-butyl acrylate) (PTBA).

Poly(2-vinylpyridine) and polystyrene are both amorphous polymers with a glass transition temperature near 100 °C. In addition, PS and PVP polymers of similar molecular weight have a nearly identical viscosity vs. temperature relationship.⁸ Nevertheless, the development of the gold particle morphology above the glass transition temperature is remarkably different for the two polymers. In particular, the coarsening rate of the particles in a PVP matrix is much lower than the coarsening rate in a PS matrix.⁶ We have characterized the PVP/Au system as a "strongly" interacting system, in that the exchange of polymer segments in intimate contact with the metal particles is very slow. The reduced rate of exchange allows for polymer molecules in contact with different particles to act as bridges between them. For sufficiently high particle concentrations, a network of bridges is formed, which retards particle diffusion, and reduces the rate at which particles can come into contact with one another in order to coalesce into a larger particle. At low particle concentrations, the average particle separation exceeds the characteristic dimensions of the polymer molecules. In this case, particle bridging is not a factor. Particle diffusion at low concentrations still takes place for strongly interacting systems, although the hydrodynamic radius of the particles may exceed the actual particle radius by an amount which is related to the polymer chain dimensions.⁷

Polystyrene and poly(2-vinylpyridine) have several disadvantages with respect to their use as model polymer matrices for studying the properties of polymer/metal nanocomposites. The PVP/Au system is so strongly interacting that particle coalescence, and particle diffusion at high particle concentrations, are essentially eliminated altogether.⁶ The strength of the PS/Au
interaction is not as high, but photo-oxidation of the PS is potentially a problem. Even very low levels of oxidation can affect the PS/Au interactions significantly. We believe these effects are responsible for the difficulties we have had obtaining reproducible results from the PS/Au system. These difficulties are avoided with the model system we are investigating here, consisting of gold nanoparticles in a poly (t-butyl acrylate) (PTBA) matrix. As with the previous studies, gold was chosen for its high atomic number and relative inertness to chemical reaction. In addition to its excellent oxidative stability, PTBA is easily spun-cast into uniform films. This polymer can also be converted to other acrylic systems, allowing for future work to probe the effects of different functional groups on the polymer-metal interactions. PTBA also has a glass transition temperature (T_g) of about 45°C, which is conveniently accessible. Finally, the PTBA/Au interactions appear to be uniquely weak. The relative lack of interaction is thought to be derived from the presence of the bulky t-butyl group, which shields the gold particles from the more interactive ester group and its delocalized \( \pi \)-bonded electrons. Molecular orbital calculations performed by Ho et al. have, for example, shown that delocalized electrons are responsible for strong interactions between an individual gold atom and a benzene ring. Despite the relatively weak interactions between gold and PTBA, significant effects due to bridging interactions between particles are observed, as described in the following sections.

EXPERIMENT

Information about the mobility of individual gold particles and the polymer molecules themselves was determined from measurements of the depth distribution of the gold particles after different annealing treatments above the glass transition temperature of PTBA. The polymers were synthesized in our lab using anionic polymerization to achieve polydispersities (the ratio of weight average to number average molecular weight) of less than 1.15. Our synthetic procedure is similar to the procedure which has been described by Fayt, et al. Diffusion experiments were conducted by creating sandwich samples of PTBA containing a buried layer of gold nanoparticles. The samples were made by spin casting 0.3 - 0.4 \( \mu \)m PTBA films of varying molecular weights onto highly polished single crystal silicon substrates. The substrates were then placed into an evaporation system, and gold was deposited on the samples. Two different evaporation techniques, thermal evaporation and electron-beam evaporation, were utilized. These techniques are illustrated in Figure 2. In thermal evaporation, the gold is resistively heated, whereas the second method uses an electron-beam to heat the sample. The morphology and diffusive properties of the gold particles obtained by these two evaporation methods were dramatically different, as discussed in more detail below. The thickness of gold on the sample for each deposition method was monitored with a quartz crystal thickness monitor. For the diffusion experiments, the equivalent thickness of gold deposited was typically between 0.4-0.5 nm. This thickness is insufficient to achieve continuous coverage, and the film actually consists of islands, approximately 3 nm in diameter, of roughly spherical shape.

Following the evaporation of the gold, another polymer film was spun-cast onto a glass slide, and the film was floated off the slide onto a water bath. This film was then placed on the silicon substrate, on top of the evaporated layer, creating a sandwich. The excess water was evaporated in vacuum at room temperature, producing a uniform sample with a gold layer buried in the center of the film. Diffusion experiments were then performed by annealing the sandwich in vacuum, at temperatures between 50-165°C, depending on the polymer molecular weight. Higher temperatures were avoided, since PTBA will degrade at \(~180^\circ \)C, and partial conversion to poly (acrylic acid) may occur at slightly lower temperatures.
Upon annealing, the particles diffuse through the polymer by Brownian motion. This motion was quantified by utilizing Rutherford Backscattering Spectrometry (RBS) as a depth profiling technique. The polymer sandwich samples are well suited for RBS, as the sensitivity to marker atoms increases as the square of the atomic number. This sensitivity allows extremely small fractions of a high mass element, such as gold, to be detected reliably while embedded in a low atomic mass matrix, such as the PTBA film. The separation in recoil energy of incident ions scattered from gold versus those scattered from the lower atomic mass constituents allows the gold concentration profile to be isolated from the signal from the substrate to a depth of ~1 μm. The samples showed extensive mass loss due to the ion beam striking the sample, but further experimentation revealed that despite the degradation of the polymer, the distribution of particles in the sample remained unaltered, allowing quantitative analysis despite the beam damage. To extract diffusion coefficients from the measured depth profiles, simulated concentration profiles were fit to the actual data. These simulated profiles corresponded to the appropriate solutions to the diffusion equation, convoluted with a Gaussian broadening function to account for the RBS depth resolution.

Finally, in order to assess the potential interplay between particle motion and polymer motion, diffusion samples were made in which the molecular weights of the polymers on either side of the gold layer were different. We refer to these experiments as "marker motion" experiments, because in addition to any diffusive broadening of the gold particle distribution, there is a net translation of the center of the distribution toward the lower molecular weight polymer. The gold particles in this case can be viewed as markers which are sensitive to the diffusive motions of the polymer molecules themselves.
RESULTS AND DISCUSSION

Gold particle Diffusion

Figure 3 shows the results of a gold particle diffusion experiment in which the polymer on either side of the gold layer was PTBA with a molecular weight of 7,000 g/mol. The sample was heated for one hour at 65 °C. The gold particle diffusion coefficient, D, in this case is $1.58 \times 10^{-14}$ cm$^2$ s$^{-1}$. A convenient way to analyze the data is by comparison to the Stokes-Einstein equation for diffusion of isolated spherical particles in a viscous medium:

$$ D = \frac{k_B T}{6 \pi \eta R} \quad (1) $$

Here $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $\eta$ is the viscosity of the medium, and $R$ is the particle hydrodynamic radius.\(^{14}\) This theory contains the implicit assumption that the viscosity of the medium is not affected by the particles themselves. It is this assumption that leads to our definition that a system which shows particle diffusion in close accord with the Stokes-Einstein prediction should be classified as ‘non-interacting,’ a system in which diffusion is present but substantially slowed compared to Stokes-Einstein predictions is ‘weakly interacting,’ and a system where diffusion is eliminated entirely (as is the case for polyvinylpyridine)\(^{6}\) is ‘strongly interacting.’ In the context of our introductory remarks concerning the segregation of metal particles to individual domains in ordered morphologies, the same interactions which cause preferential segregation into one of the domains are also responsible for hindering the motion of particles in that domain.

In Figure 4, the measured diffusion coefficients are plotted versus temperature and compared to predictions from the Stokes-Einstein equation, using effective values of the hydrodynamic radius to force agreement with the predictions. The viscosity was determined separately for each polymer molecular weight and temperature (in the absence of gold particles) by oscillatory shear rheometry. Our analysis here in terms of the Stokes Einstein equation is instructive. Note that the values of the effective hydrodynamic radius determined in this way are quite large, varying from 70 nm for PTBA with a molecular weight of 7000 g/mol, up to 1000 nm for PTBA with a molecular weight of 100,000 g/mol. The highest of these values is nearly three orders of magnitude larger than the actual particle radii. These radii are approximately 1 nm, and even with the presence of some particle coarsening should not exceed 10nm.\(^{6}\) These large effective hydrodynamic radii are compelling evidence of the formation of bridging interactions between particles.
Figure 3: Typical gold particle concentration profiles before annealing (crosses) and after annealing for 1 hour at 65°C (solid line). The width of the distribution prior to annealing is a measure of the RBS depth resolution.

Figure 4: Gold particle diffusion coefficient vs. temperature for three polymer molecular weights. $M = 7,000$ g/mol (O), $M = 77,000$ g/mol ($\Delta$), and $M = 100,000$ g/mol (+). The Stokes-Einstein predictions are indicated for each polymer. The effective hydrodynamic radii are 70 nm (solid line), 400nm (upper dashed line), and 1000nm (lower dashed line).
A comparison of the length scales of a polymer strand and the interparticle spacing shows that even for relatively short chains such as the 7,000 g/mol PTBA, bridging interactions are likely. The statistical segment length, $a$, defined as the effective length of a monomer in a random walk model of polymer chain dimensions, is roughly 0.7 nm for PTBA. The root-mean-square end-to-end distance, $R_0$, for a polymer molecule with a molecular weight of $M$ is $a(M/M_0)^{1/2}$, where $M_0$ is the repeat unit molecular weight. For PTBA, $M_0 = 128$ g/mol, from which we obtain $R_0 = 5.2$ nm for $M = 7000$ g/mol, as compared with $R_0 = 17$ nm for $M = 77,000$ g/mol, and $R_0 = 20$ nm for $M = 100,000$ g/mol. The average particle separation, $L$, will depend on the size and distribution of the particles. For particles which reside in a two-dimensional layer, simple geometric arguments yield $L = (2r)^{3/2}h^{1/2}$, where $r$ is the particle radius and $h$ is the equivalent thickness of the metal particle layer. For our samples $r \sim 1$ nm and $h \sim 0.4$ nm, yielding $L \approx 4.4$ nm. If the particles are distributed through the thickness of a polymer film of thickness $H$, the scaling changes to $L = 2r(H/h)^{1/3}$. For a 100 nm film $L = 12.6$ nm, which exceeds the end-to-end distance for only the lowest molecular weight polymer in our experiments. Clearly, at a fixed value of $L$, the importance of bridging interactions will increase as the polymer molecular weight increases. This effect is evident in our experiments, where the effective hydrodynamic radii of the gold particles increase dramatically as the polymer molecular weight increases. Also, we have found in preliminary experiments that the effective hydrodynamic radius decreases as the particles diffuse, and does not necessarily remain constant throughout a given diffusion experiment. The decrease in effective particle radius can be attributed to increases in $L$ as the particles diffuse throughout the film. Increases in $L$ due to particle coarsening may also play a role here. Other experiments using colloidal gold suggest that reducing the concentration of particles to the point where $L$ far exceeds typical polymer chain dimensions leads to fewer bridging interactions and better agreement with the Stokes-Einstein predictions based on actual particle dimensions.

Marker motion experiments

Figure 5 shows a representative sample geometry for the marker motion experiments. In these experiments, gold particles were sandwiched between PTBA polymers with very different molecular weights (420,000 g/mol vs. 7,000 g/mol). Two types of samples were prepared. For the first type of sample, the higher molecular weight polymer was spun-cast on the silicon substrate. Gold was then evaporated on this sample, and the low molecular weight film was floated on top of the higher $M$ film. The second sample had the reverse of this geometry, with the lower molecular weight film directly against the substrate. Both samples were annealed for 30 minutes at $85^\circ$C, and in both cases the interface moved toward the low molecular weight layer.

Several factors determine the rate of gold particle motion in the marker motion experiments. The simplest approaches assume that the gold particles are "inert" markers which do not alter the diffusive behavior of the polymers. In this case the rate of marker motion is determined by the relative fluxes of molecules in the two directions across the interface. Suppose that the fast-diffusing, low molecular weight molecules exist at higher concentrations to the right of the markers, so that the flux of material to the left will be higher than the flux of material to the right. The net flux of atoms to the left leads to the buildup of compressive, osmotic stresses to the left of the markers. These stresses reduce the net flux of molecules to the left, unless these stresses are able to relax on the time scale of the experiment. From a theoretical standpoint, two limiting cases have been considered. In the "slow" theory of mutual diffusion, it is assumed that these stresses cannot relax over the timescale of the experiment, so that the net fluxes to the right and to the left of the markers are equal to one another. In this case there is no net motion of the
markers. In the "fast" theory of mutual diffusion, the opposite assumption is made, i.e., that the osmotic stresses relax to zero very quickly, so that these stresses do not affect the marker motion. In this case the marker motion is determined primarily by the faster diffusing species. The displacement of the markers, \( \Delta x_m \), varies with the square root of the diffusion time according to the following equation:

\[
\Delta x_m = C \sqrt{D^* t}.
\]

Here \( C \) is a constant related to the ratio of diffusion coefficients of the two polymer layers, \( D^* \) is the tracer-diffusion coefficient of the lower molecular weight polymer, and \( t \) is the annealing time. In our case, the diffusion constants of the two polymers are very different, and \( C \) can be assumed to be equal to the limiting value of 0.48 for a divergent ratio of diffusion coefficients. In this manner we obtain \( D^* = 8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1} \) for the sample with the higher molecular weight polymer as the bottom layer, and \( D^* = 9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1} \) for the sample with the high molecular weight polymer as the top layer. This comparison indicates that there is no preference for the markers to move toward the substrate or toward the free surface. Evaluating the marker motion as a function of time reveals that the marker displacement scales as \( t^{1/2} \). Figure 6 shows the data from a series of marker motion experiments carried out at 60°C. A best fit to the data produces \( D^* = 2.52 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1} \).

![Schematic representation of the marker motion experiments.](image)

**Figure 5**: Schematic representation of the marker motion experiments.

The central quantity relating diffusive and rheological behavior of polymer melts is the monomeric friction factor, \( \zeta_0 \). The tracer diffusion coefficient of a relatively low molecular weight polymer molecule is given by the following expression: 17

\[
D^* = \frac{k_B T M_0}{M \zeta_0}
\] (2)
where it has been assumed that \( M \) is low enough so that the diffusing molecule does not form entanglements with molecules in the polymer matrix. This assumption is certainly valid for PTBA with \( M = 7,000 \) g/mol, since the entanglement molecular weight of this polymer is near 20,000 g/mol. The monomeric friction factor can also be related to the zero shear viscosity of an unentangled polymer melt through the Rouse theory of polymer dynamics.\(^8\) In this context \( \zeta_0 \) is given by the following expression:

\[
\zeta_0 = \frac{36\eta_0 M_0^2}{MN_{\text{av}} \rho a^2}
\]  

(3)

where \( \rho \) is the bulk density of PTBA and \( N_{\text{av}} = 6.02 \times 10^{23} \). Previous comparisons of polymer self-diffusion coefficients and melt viscosities in the unentangled regime have confirmed that friction factors determined from these two types of experiments are quite consistent with one another.\(^{16,17,19}\) Deviations in the friction factors in our case can therefore be attributed either to the presence of the gold particles, or to deviations from the prediction of the fast theory of mutual diffusion which we have used here. The friction factor obtained from rheological data between 60 °C and 160 °C is given by \( \log \zeta_0 = A + B/(T - T_{\text{ref}}) \) with \( A = -12.4, B = 706 \) and \( T_{\text{ref}} = -10.3^\circ \text{C} \). At 60 °C, we obtain \( \zeta_0 = 4.7 \times 10^{-3} \) g s\(^{-1} \) from the bulk viscosity of the polymer. The calculated friction factor at 60 °C from the marker motion experiments is \( \zeta_0 = 3.34 \times 10^{-2} \) g s\(^{-1} \).

The comparison made above indicates that the friction factor obtained from the marker motion experiments is seven times larger than the value obtained from the viscosity measurements. One possible interpretation of this discrepancy is that the gold particles are not necessarily acting as "inert" markers, but that they somehow hinder the diffusion of the low molecular weight PTBA molecules. Recall, however, that our analysis is based on the "fast" theory of polymer interdiffusion, where osmotic pressure gradients in the sample are assumed to relax very quickly. In fact, the relaxation time for the high molecular weight polymer (obtained as the ratio of viscosity to plateau modulus) is approximately 2 days at 60 °C, which is several times longer than the longest annealing times in our experiments. Some slowdown of the marker motion compared to the predictions of the fast theory is obviously expected, as this experiment was almost certainly conducted in the crossover regime between the validity of the fast and slow theories of mutual diffusion. An increase of the "effective" friction factor by a factor of seven seems plausible. At this point, we can only conclude that the observed marker motion is potentially consistent with the ability of polymer molecules to pass through a relatively concentrated dispersion of metal particles, provided that these particles are produced by thermal evaporation.
Figure 6: Time dependence at 60 °C for thermally evaporated gold particles sandwiched between PTBA layers with molecular weights of 7,000 g/mol and 420,000 g/mol. The equivalent thickness of the gold layer is 0.4 nm.

Very different results were obtained when the gold particles were produced by electron-beam evaporation. In this case, no diffusion or marker motion was observed for a gold particle layer with an equivalent thickness of 0.4 nm. In this case, not only are the bridging interactions between particles strong enough to eliminate any particle diffusion, but motion of polymer molecules through the gold layer is inhibited as well. One potential explanation for this is that the gold does not exist as a layer of discrete particles, but exists as a continuous gold film with a thickness of only 0.4 nm. This explanation does not seem likely to us, given that continuous gold films on inorganic glasses are only formed for thicknesses of several nanometers. Nevertheless, we have not been able to rule out this possibility explicitly. Preliminary measurements of the optical adsorption spectra of the gold films indicate that the particle size is, at the very least, considerably smaller for the gold films produced by electron-beam evaporation than for the films produced by thermal evaporation. Our conclusions here are based on the nature of the plasmon resonance peak near 550 nm which is characteristic of nanometer-scale metal particles. This adsorption maximum is reduced substantially in intensity for the films produced by electron-beam evaporation, which is the expected result for a very small particle size, perhaps approaching the continuous film limit. Clearly the structure and properties of the gold films depend not only on the polymer, but on the deposition method as well.

CONCLUSIONS

The gold/PTBA system is an ideal system for studying the behavior of concentrated metal particle dispersions, where the distance between particles is less than the dimensions of the polymer molecules. Interparticle bridging interactions arising from the slow exchange kinetics of polymer molecules in contact with different particles significantly retard particle diffusion in these systems. Polymer/metal interactions in the gold/PTBA system are “weak, in that measurable
diffusion coefficients are obtained for the gold particles. Nevertheless, these diffusion coefficients are two to three orders of magnitude less than predictions based on the Stokes-Einstein equation for particle diffusion in a viscous medium. For gold particles produced by thermal evaporation, the temperature dependence of particle diffusion follows the temperature dependence of the bulk viscosity, but the effective hydrodynamic radius of the gold particles is up to 50 times larger than the end-to-end distance of the polymer molecules, which is in turn larger than the gold particles themselves. The long relaxation time of the high molecular weight polymer used in our marker motion experiments makes it difficult for us to assess the degree to which diffusion of polymer molecules through the metal particle dispersions is actually hindered. At any rate, any potential slowdown of polymer diffusion is certainly much less than the slowdown of metal particle diffusion, at least for the thermally evaporated particles. For gold particles produced by e-beam evaporation, particle diffusion is eliminated altogether, and polymer molecules are not able to diffuse throughout the gold layer. Our overall conclusion is that particle mobility at high concentrations in polymer melts is dramatically reduced, even in systems where the polymer/metal interactions are quite weak.

REFERENCES