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Synthesis of Palladium Nanoclusters within Spherical Microdomains in Films Made from Block Copolymer/Homopolymer Blends

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Palladium-containing block copolymers of general formula $[Pd(Cp^N)(PA)]_n[MTD]_m$ (Cp^N = *endo*-2-(cyclopentadienylmethyl)norborn-5-ene, PA = η^3-1-phenylallyl, and MTD = methyltetracyclododecene) that exhibit a spherical morphology when blended with polyMTD homopolymer have been prepared by living ring-opening metathesis polymerization (ROMP) using $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (Ar = 2,6-diisopropylphenyl) as the ROMP initiator. Mild heating of the polymer films under hydrogen leads to the formation of small palladium clusters (<100 Å) whose sizes and size distributions vary with the size of the metal-containing spherical microdomains.

Introduction

We have been developing a new method for synthesizing small metal[1–3] or metal sulfide[4,5] particles within diblock copolymer films. In this method a metal complex (or two) is attached to each repeating unit in one of the blocks of the diblock copolymer. When a film is cast the thermodynamic incompatibility of the blocks cause the diblock copolymers to separate into microphases that have a regular size and spacing between the microphases.[6–9] The metal can be introduced into the polymer either by preparing a norbornene derivative that can be polymerized subsequently or by coordinating the metal to the appropriately functionalized diblock in the process of casting the polymer film. In this manner metal or semiconductor (metal sulfide) nanoclusters less than 100 Å have been synthesized within metal-containing polymer microdomains.

In principle it should be possible to prepare a single cluster of a desired size within a spherical microdomain, the only microphase whose size is limited in three dimensions. The number of metal atoms formed in a spherical microphase will be determined by the number of metal-containing repeat units in a given block times the number of blocks that are used to form the microphase (essentially monodisperse in the best case). In a recent communication[3] we reported that under ideal conditions a single silver cluster (~55 Å in diameter) can be synthesized in high yield within every spherical microdomain of a spherical microphase-separated film. The use of a phosphine-containing diblock copolymer to incorporate the silver precursor has allowed us to show (by electron microscopy) that the clusters nucleate and grow within the original microdomains. Here we report further studies on the synthesis of palladium nanoclusters within polymer films that display a spherical morphology. In particular, we have been able to study the variation in metal cluster size with microdomain size. The polymer films were prepared by blending a palladium-containing diblock copolymer of general formula $[Pd(Cp^N)(PA)]_n[MTD]_m$ (Cp^N = *endo*-2-(cyclopentadienylmethyl)norborn-5-ene, PA = η^3-1-phenylallyl, MTD = methyltetracyclododecene[10]) with polyMTD homopolymer. The clusters were generated by treating the film with hydrogen at mild elevated temperatures. The results are compared to a polymer film that shows no microphase separation but has the same percent metal content.

Experimental Section

Monomer synthesis, polymerizations, and analytical protocol have been described in detail elsewhere.[2]

Synthesis of $[Pd(Cp^N)(PA)]_n[MTD]_{375}$. MTD (800 mg, 4.59 mmol) was dissolved in 20 g of toluene, and 12.2×10^{-3} mmol of $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (from a stock solution) was added with rapid stirring. After 25 min, the solution was divided equally into four vials, freshly synthesized $Pd(Cp^N)(PA)$ was added to the solutions (0, 0.11, 0.23, and 0.46 mmol, respectively), and the reactions were stirred for 0, 20, 25, and 35 min, respectively. The polymers were then capped by adding excess benzaldehyde (5 mg, reaction time 45 min), precipitated in pentane (diblocks) or methanol (MTD homopolymer) and dried in vacuo for 48 h; the yields were quantitative. $[Pd(Cp^N)(PA)]_2[MTD]_{198}$ and $[MTD]_{200}$ were synthesized in the same manner.

Molecular Weight Determination. The number average molecular weight (M_n) of the polymers was determined by gel permeation chromatography (GPC) relative to polystyrene standards in tetrahydrofuran using refractometer and UV–vis detectors (see Table I).

Film Casting. Polymer films (ca. 3 wt %) were cast from benzene solution in a drybox under a nitrogen atmosphere over 5–8 days and then placed under vacuum for at least 2 days prior to analysis.

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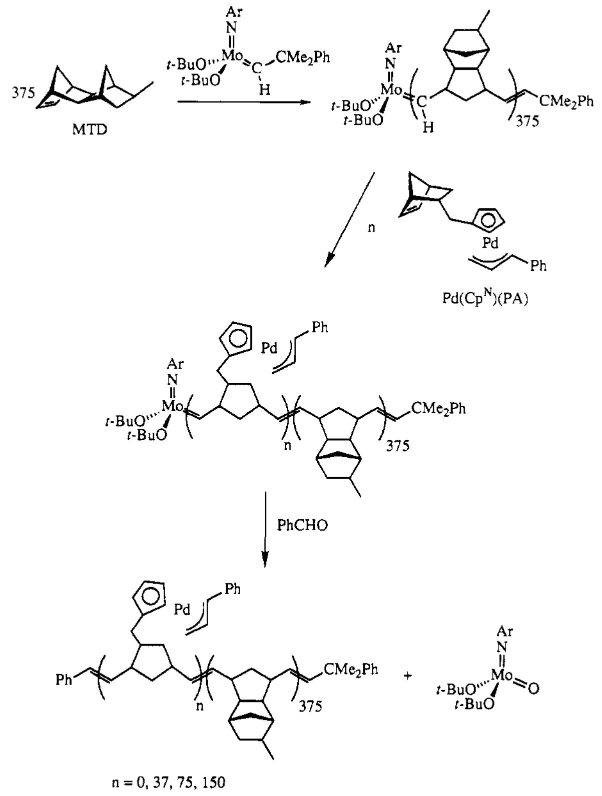
Scheme I. Synthesis of $[Pd(Cp^N)(PA)]_n[MTD]_{375}$ Diblocks



Density Measurement. A $[Pd(Cp^N)(PA)]_{100}$ homopolymer was synthesized in similar fashion as described above, purified by precipitation in pentane, and dried under high vacuum for 3 days. The polymer was crushed into small pieces and its density measured by the floatation method in H_2O/KI solutions. The observed density of 1.35 g/cm^3 did not change when the polymer was dried further.

Cluster Synthesis and Characterization. The bulk polymer films (~0.3 mm thick) were treated with hydrogen under 5 bar in a stainless steel reactor immersed in a heated oil bath. (Temperatures are specified in the text). To ensure uniform heating, the sample was placed in the reactor with a few milliliters of water. No physical change in the polymers was apparent. Thin sections (~300 Å) of the polymer films (before and after reduction) were obtained by microtomy. The microtomed sample was placed on a copper grid and analyzed by transmission electron microscopy on a JEOL 200 CX machine operating at 200 kV. Details of the decomposition of $Pd(Cp^N)(PA)$ under hydrogen have been reported elsewhere.[2] Analysis of the reduced samples by X-ray powder diffraction revealed only a weak (111) peak that could be ascribed to palladium metal, most probably because of the low metal content. For the same reason reliable data on the crystallite size and size distribution could not be obtained.

Results and Discussion

Polymer Synthesis. Red palladium-containing diblock copolymers were prepared by sequential ring-opening metathesis polymerization (ROMP, Scheme I) of MTD and $Pd(Cp^N)(PA)$ using $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$[11] (Ar = 2,6-diisopropylphenyl) as the initiator. The diblock was then capped with benzaldehyde via a Wittig-like reaction. The measured (versus polystyrene) and calculated molecular weights and the polydispersity index of the resulting diblock copolymers ($[Pd(Cp^N)(PA)]_n[MTD]_{375}$, n = 37, 75, 150) are given in Table I. (The subscript refers to the number of equivalents of monomer used per equivalent of initiator). A plot of the measured molecular weight (relative to polystyrene standards) against the number equivalents of palladium-containing monomer added to living $[MTD]_{375}$ gives a straight line consistent with the living characteristics of the polymerization reaction (Figure 1). The diblocks were then blended with $[MTD]_{200}$ homopolymer in benzene so as to give a blend that contained 2 wt % of palladium-block in each case. The films were then static-cast. Thin sections (~300 Å) of the cast films were prepared and analyzed by transmission electron microscopy (TEM). The micrographs (Figure 2a–c) revealed spherical metal-containing microdomains whose size, as expected, decreased with a decrease in the length of the metal-containing block (Table II). A polymer having the composition $[Pd(Cp^N)(PA)]_2[MTD]_{198}$ (2 wt % of $Pd(Cp^N)(PA)$) was also prepared and was cast in the absence of added homopolymer. In this case the metal-containing block is not large enough to induce microphase separation and a homogeneous polymer film is the result according to TEM (Figure 2d). All films had the same metal content (0.54%).

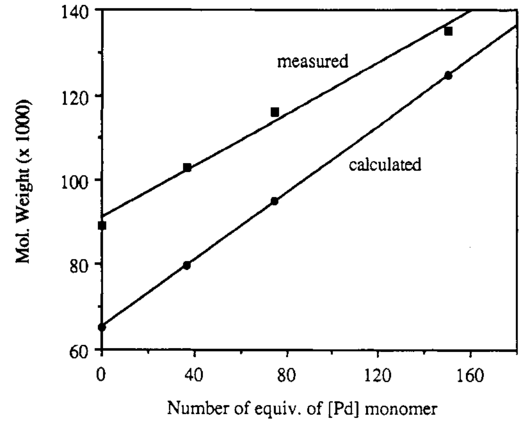


Figure 1. Calculated and measured (relative to polystyrene standards) molecular weights of $[Pd(Cp^N)(PA)]_n[MTD]_{375}$ (n = 0, 37, 75, 150).

Table I. GPC Analyses of Polymers

polymer	calcd M_w	M_n	polydispersity
$[Pd(Cp^N)(PA)]_{37}[MTD]_{375}$	79 960	103 000	1.10
$[Pd(Cp^N)(PA)]_{75}[MTD]_{375}$	94 960	116 000	1.11
$[Pd(Cp^N)(PA)]_{150}[MTD]_{375}$	124 570	135 000	1.17
$[MTD]_{375}$	65 350	89 000	1.06
$[Pd(Cp^N)(PA)]_2[MTD]_{198}$	35 295	39 000	1.06
$[MTD]_{200}$	34 850	39 500	1.03

Cluster Synthesis. When the polymer film prepared from the blend $[Pd]_{37}[MTD]_{375}/[MTD]_{200}$ was heated at 90 °C under 5 bar of hydrogen for 3 days, the film changed from red to black. The formation of palladium clusters was evident by TEM analysis of a thin section of the film. A representative micrograph is shown in Figure 3. The clusters in Figure 3 are well-separated from one another and have a mean diameter of 33 Å with a standard deviation of 7.1 Å. A calculation based on the density of the metal-containing homopolymer (1.35 g/cm^3) predicts that if one cluster is formed within one microdomain its size would be ~0.3 times the size or the original microdomain, assuming that the original microdomain is comprised of metal-containing segments only. The relatively narrow size distribution (Figure 4) of the clusters suggests that a single cluster formed within every microdomain. The cluster size distribution is larger than we had hoped, probably because the metal-containing microdomains are

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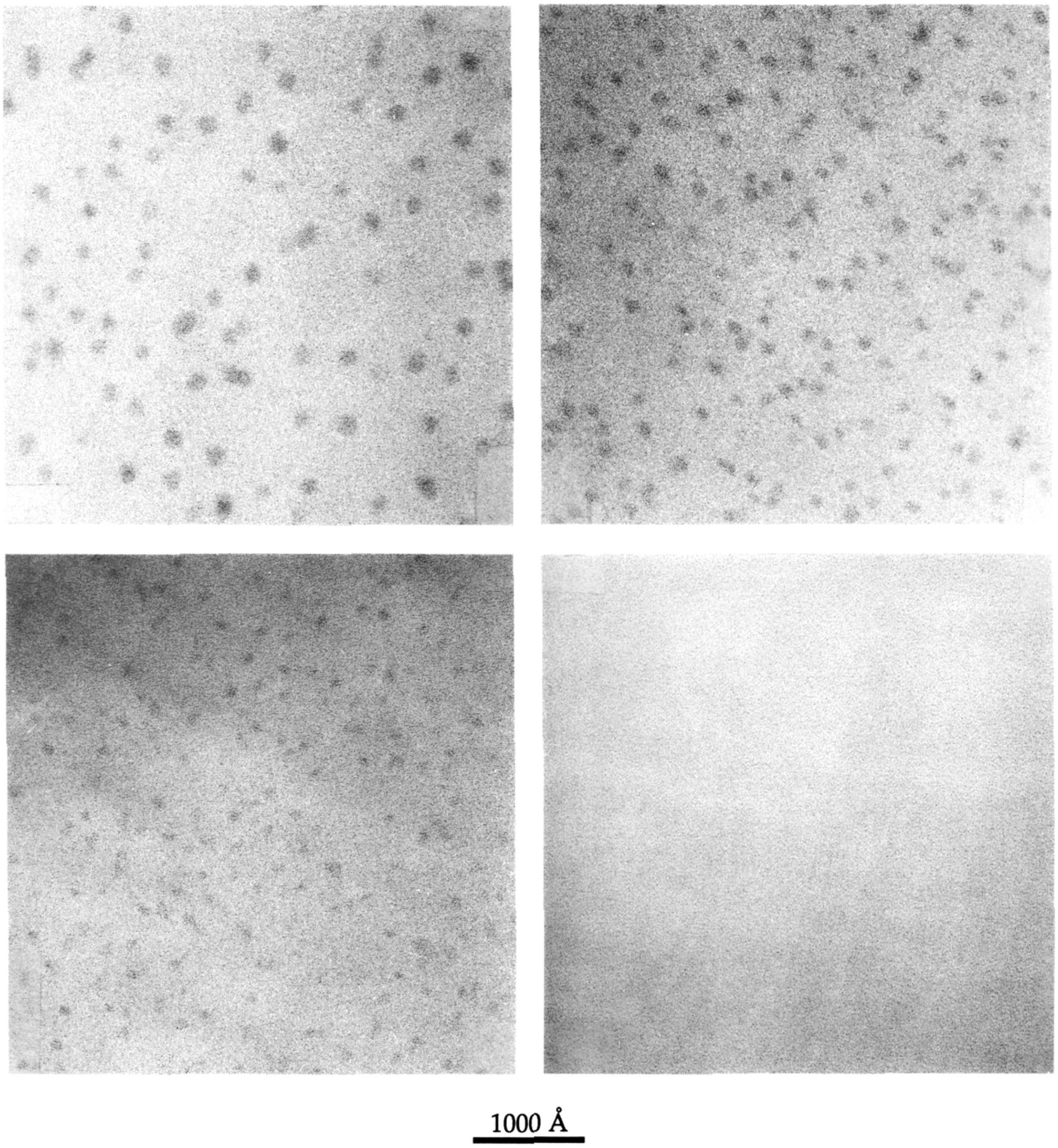

Figure 2. Electron micrographs of polymer films before reduction: (a) $[Pd(Cp^N)(PA)]_{150}[MTD]_{375}/[MTD]_{200}$ (top left); (b) $[Pd(Cp^N)(PA)]_{75}[MTD]_{375}/[MTD]_{200}$ (top right); (c) $[Pd(Cp^N)(PA)]_{37}[MTD]_{375}/[MTD]_{200}$ (bottom left); (d) $[Pd(Cp^N)(PA)]_2[MTD]_{198}$ (bottom right).

Table II. Microdomain Size (Å) Estimated by TEM

polymer	$[Pd]_{150}[MTD]_{375}/[MTD]_{200}$	$[Pd]_{75}[MTD]_{375}/[MTD]_{200}$	$[Pd]_{37}[MTD]_{375}/[MTD]_{200}$	$[Pd]_2[MTD]_{198}$
microdomain size (Å)	220	150	100	homogeneous

not monodisperse. Unfortunately, it was difficult to determine the polydispersity of the original metal-containing microdomains by TEM for experimental reasons, and therefore we can only estimate that the standard deviation is <20%. A sample prepared by heating the $[Pd]_{37}[MTD]_{375}/[MTD]_{200}$ film to 150 °C under 5 bar of hydrogen for 3 days was the same as that shown in Figure 3. Therefore differences in relative rates of nucleation and growth within this temperature range, temperatures that are still below the glass transition temperature of the polyMTD matrix (ca. 215 °C), are not translated into obvious differences in cluster size and distribution. This approach is similar to that in which single silver clusters were prepared within phosphine-containing spherical microdomains.[3]

$[Pd]_{75}[MTD]_{375}/[MTD]_{200}$ and $[Pd]_{150}[MTD]_{375}/[MTD]_{200}$ polymers heated at 90 °C under 5 bar for 3 days under similar conditions yielded clusters that had mean diameters estimated at about 40 Å (range 25–60 Å) and 45 Å (range 25–75 Å), respectively. Therefore the trend is toward an increase in the number of Pd atoms per cluster, although the relatively broad range in each case prevented an accurate verification of the size increase. The TEM micrographs (Figures 5 and 6) reveal that some clusters are in groups of 2–5, a situation that is most prominent in the sample prepared from $[Pd]_{150}[MTD]_{375}/[MTD]_{200}$

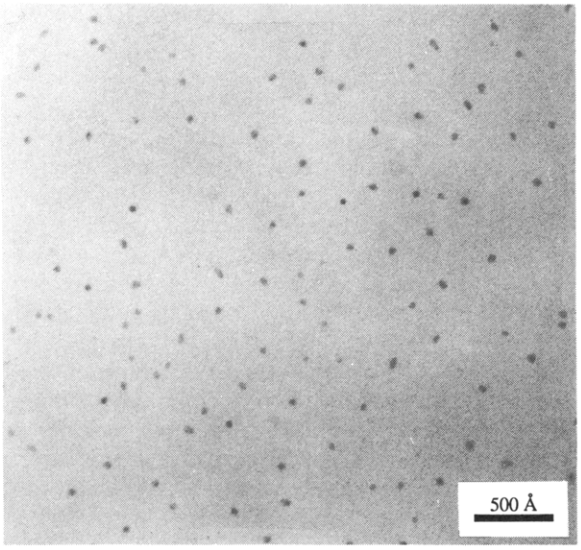

Figure 3. Electron micrograph of $[Pd(Cp^N)(PA)]_{37}[MTD]_{375}/[MTD]_{200}$ after reduction at 90 °C.

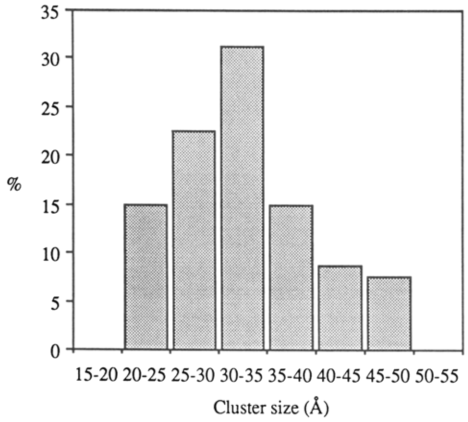

Figure 4. Cluster size distribution in polymer $[Pd]_{37}[MTD]_{375}/[MTD]_{200}$ after reduction at 90 °C. Total number of clusters = 80, mean diameter = 33 Å, and standard deviation = 7.1 Å (20%).

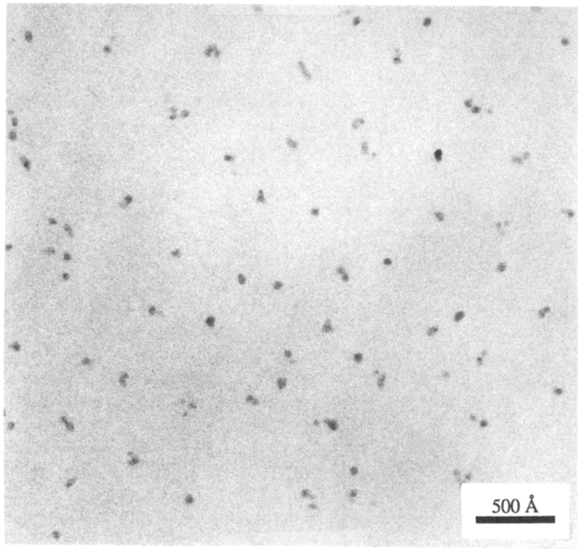

Figure 5. Electron micrograph of $[Pd(Cp^N)(PA)]_{75}[MTD]_{375}/[MTD]_{200}$ after reduction at 90 °C.

(Figure 6). This result is most easily explained if several clusters form within each microdomain. The formation of more than one cluster per microdomain as the microdomain size is increased is a logical consequence of the greater amount of metal available within each microdomain and the kinetic restraint by the polymer matrix within the microdomain on the mobility of metal atoms or small clusters. These factors encourage nucleation to begin at more than one site and result in a broader distribution of cluster sizes. We note also that the size of the clusters is limited, which suggests that little palladium can migrate from one microdomain to another through the polyMTD. Further heating did not cause the clusters to aggregate. Cluster sizes and size distribution were essentially the same in films prepared at 150 °C instead of 90 °C, although in the films prepared at 150 °C the clusters appear to be more spread out, presumably because of enhanced cluster mobility at the higher temperature.

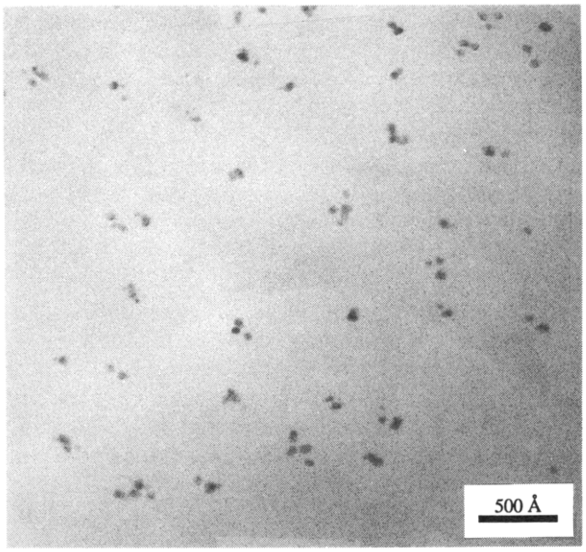

Figure 6. Electron micrograph of $[Pd(Cp^N)(PA)]_{150}[MTD]_{375}/[MTD]_{200}$ after reduction at 90 °C.

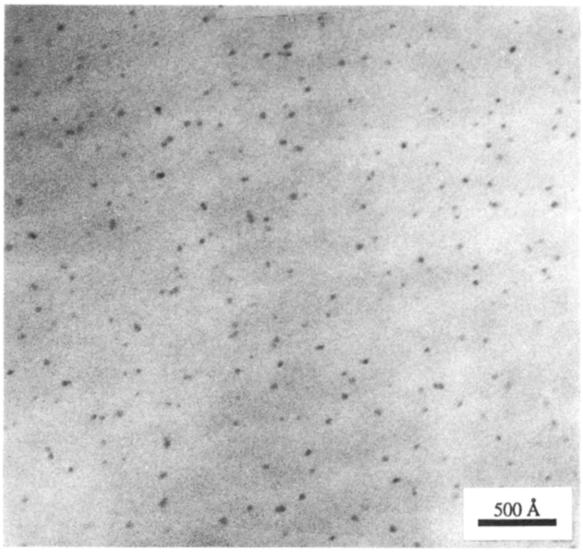

Figure 7. Electron micrograph of $[Pd(Cp^N)(PA)]_2[MTD]_{198}$ after reduction at 120 °C.

Although nucleation and growth are independent processes that occur on different time scales, both are related to the rate of decomposition of the metal precursors.[12,13] Attempts to reduce the rate of nucleation by reducing the

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rate of decomposition were unsuccessful. At room temperature the decomposition was indeed very slow, but the mobility of atoms and small cluster also was reduced; therefore again several clusters (<20 Å in size) formed within each microdomain. In another experiment lasting 5 days the temperature was kept at 120 °C, but the hydrogen pressure was reduced to 1.5 bar; near the surface of the polymer film clusters were formed which were similar in size and size distribution as those prepared in reductions conducted at 5 bar, but inside the polymer decomposition seemed to be incomplete.

The synthesis of clusters within a film made from $[Pd]_2[MTD]_{198}$ homopolymer (having the same total metal content as the previous polymer films) was also investigated. When the homopolymer film was heated at 90 °C under 5 bar of hydrogen, no palladium clusters were visible by TEM analysis of a thin section of the film. Only when the sample was heated at 120 °C or above could palladium clusters be observed, but the clusters were less than ~25 Å in diameter (Figure 7). The explanation seems to be straightforward. At 90 °C the limited mobility of the atoms or small clusters would give rise only to very small clusters (<15 Å) that could not be observed by TEM, whereas at 120 °C mobility is enhanced sufficiently so that the clusters can grow. However, they remain very small since the local concentration of metal is relatively low.

Conclusion

Synthesis of metal-containing block copolymers and control of their composition and molecular weight has allowed us to confine metal complexes within spherical microdomains. Reduction of the metal complexes in the polymer films at temperatures below the glass transition temperature of the matrix (polyMTD) yielded clusters whose size and size distribution can be controlled to a significant degree by controlling the amount of metal available within that microdomain. Although we can document that the size of the cluster increases as the size of the microdomain (amount of metal available) increases, multiple nucleation eventually results within a single microdomain, giving rise to several clusters instead of a single larger cluster.

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