shoulder at 500–650 nm in CH_3CN; thus, the color of the solution is reddish-brown. Reduction of **1** to $\mathbf{1H_2}$ (quinol form) by methylhydrazine caused the complete disappearance of the absorptions but gave a new one at 306 nm ($\epsilon = 1.62 \times 10^4\ M^{-1}\ cm^{-1}$).[16] These spectra of **1** and $\mathbf{1H_2}$ resemble in shape those of MADH from *Paracoccus denitrificans* ($MADH_{ox}$, 440 nm; $MADH_{red}$, 326 nm).[5a] In the resonance Raman spectrum of **1**,[17] strong peaks were detected at 1620 (C=O vibration mode), 1570, 1455, 1170, 1146, 1064, and 955 cm^{-1}, which are also closely related to those of TTQ in the native enzymes.[9]

It should be emphasized that model compound **1** acts as a very efficient turnover catalyst in the oxidation of benzylamine under aerobic conditions. *N*-Benzylidenebenzylamine was obtained in the reaction of **1** (1.0 mM) and benzylamine (100 mM) under O_2 atmosphere: 1500% (based on **1**) in CH_3CN after 8 h and 5000% in CH_3OH after 10 h.[18] Mechanistic details and structure–reactivity relationships of the amine oxidation reaction are now under investigation.

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Supplementary Material Available: Listings of experimental details of the synthetic procedures and copies of ^1H NMR, ^{13}C NMR, IR, mass, UV–vis, and resonance Raman spectra and a cyclic voltammogram of **1** (13 pages). Ordering information is given on any current masthead page.

(16) Quinol $\mathbf{1H_2}$ was easily isolated from the reaction of **1** and methylhydrazine; see the supplementary material.
(17) The resonance Raman spectrum of **1** was obtained by using 457.9-nm excitation (100 mW) (KBr disk sample).
(18) The aerobic oxidation of benzylamine was performed by the same method reported earlier: Itoh, S.; Mure, M.; Ogino, M.; Ohshiro, Y. *J. Org. Chem.* **1991**, *56*, 6857.

Synthesis of Single Silver Nanoclusters within Spherical Microdomains in Block Copolymer Films

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Recently we have been able to synthesize silver,[1] gold,[1] palladium,[2] and platinum[2] nanoclusters in lamellar or cylindrical microphase-separated precursor diblock copolymer films in which metal complexes initially were attached to the monomer comprising one block of the block copolymer. However, the greatest control over the number of atoms or molecules in a cluster should be possible in spherical microdomains. Synthesis of metal clusters in spherical microdomains is related to synthesis of metal and metal sulfide clusters in solution within micelles[3-6] and vesicles.[7]

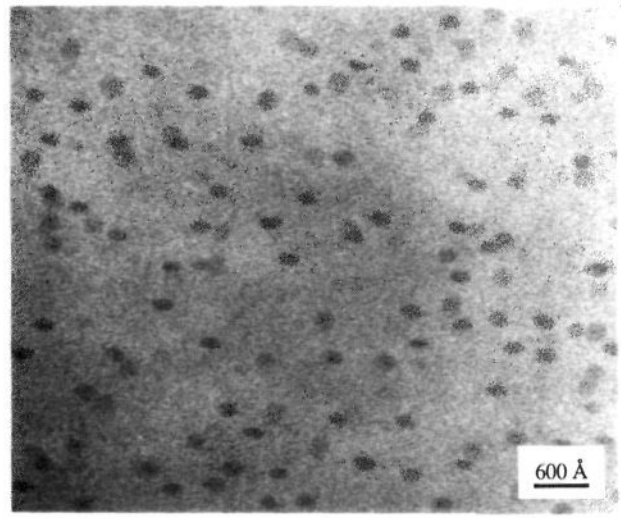
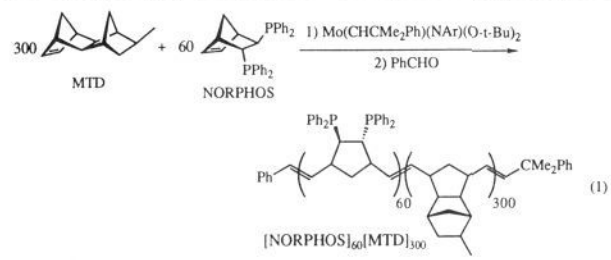


Figure 1. Electron micrograph of Ag-1 (JEOL 200 CX at 200 kV).

We report here that polymer films containing evenly-dispersed silver-containing spherical microdomains can be prepared, and that upon heating these films a single silver cluster (mean diameter <100 Å) forms within each microdomain.

A functionalized phosphine-containing diblock copolymer having the composition $[NORPHOS]_{60}[MTD]_{300}$[8] (NORPHOS[9] = racemic 2-*exo*-3-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptene; MTD = methyltetracyclododecene; eq 1) was prepared by sequential ring-opening metathesis polymerization of MTD and NORPHOS using $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$[10,11] (Ar = 2,6-$C_6H_3$-*i*-$Pr_2$) as the initiator. (The procedure has been described elsewhere.[2]) The diblock was dissolved in benzene, and 2 equiv of Ag(Hfacac)(COD)[12] (COD = 1,5-cyclooctadiene; Hfacac = $[CF_3C(O)CHC(O)CF_3]^-$) per NORPHOS was added. $[MTD]_{200}$ homopolymer (PDI (polydispersity index) = 1.03) was then added in order to yield a polymer mixture containing 3 wt % of the silver-containing block. Films (ca. 0.4 mm thick) were cast by slowly evaporating the solvent under dinitrogen in the dark over a period of 5–8 days.



$$[NORPHOS]_{60}[MTD]_{300} \xrightarrow[-\,120\ COD]{120\ Ag(Hfacac)(COD)} [Ag_2(Hfacac)_2(NORPHOS)]_{60}[MTD]_{300} \quad (2)$$

Thin sections (ca. 400 Å microtomed from the bulk) of the colorless polymer films were analyzed by transmission electron microscopy (TEM). A micrograph of $[Ag_2(Hfacac)_2(NORPHOS)]_{60}[MTD]_{300}/[MTD]_{200}$ (Ag-1; Figure 1) shows silver-

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(8) The polymers have been isolated quantitatively and purified by double precipitation in pentane. GPC analysis of $[NORPHOS]_{60}[MTD]_{300}$ gave M_n = 70000 (calcd 80030) vs polystyrene with PDI = 1.07. DSC analysis revealed a T_g at ca. 177 °C (for poly(NORPHOS)) and 215 °C (for poly(MTD)).
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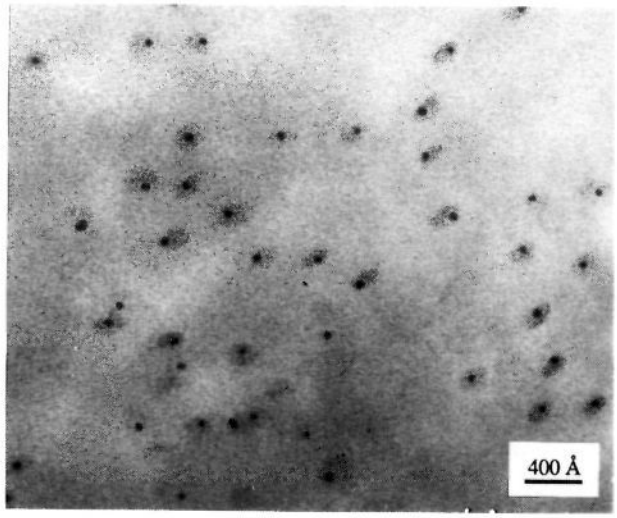

Figure 2. Electron micrograph of Ag-1 after thermal treatment. The gray areas surrounding each particle are the phosphorus-rich original microdomains.

containing microdomains ca. 180 Å in diameter. Analysis by X-ray fluorescence on a scanning transmission electron microscope (STEM) confirmed the presence of silver and phosphine within the spherical microdomains only.

The color of the Ag-1 film changed to yellow and then to red-orange upon heating to 90 °C in water for 5 days. (The relationship of the color to the plasmon frequency of the silver particles is uncertain at this point because a sample of poly(MTD) also changes slowly to yellow-orange when heated under similar conditions.) A TEM micrograph of a ca. 200 Å thick (microtomed) section (Figure 2) revealed that approximately spherical silver clusters formed within the original microdomains and that usually only one cluster is found in each microdomain. The residual phosphorus atoms provide enough contrast to image the dimensions of the original microdomain. The clusters have mean diameters of 55 Å with a standard deviation of about 20% and did not grow larger upon further heating of the sample. X-ray fluorescence microprobe analysis performed on the STEM confirmed that the clusters were located within the phosphine-containing microdomains and that decomposition of the silver complexes was complete. Although the narrow size distribution of the clusters is consistent with one cluster growing within each microdomain, a few clusters (ca. 1% or less) were found to be >100 Å in diameter, a result that would require either that the microdomain in which they originate be >310 Å in diameter[13] or that silver atoms or small clusters migrate through the MTD from one microdomain to the other. When the sample was heated at 120 °C, a much broader size distribution of clusters was observed. The phosphine centers within the microdomains may assist cluster growth, but cluster mobility through the poly(MTD) matrix between microdomains is likely to be severely restricted once the cluster reaches a certain size.

Observation of lattice fringes [(111) planes] by high-resolution TEM suggests that the particles have the same structure as the bulk metal and many of them actually are single crystals. The crystalline nature of the clusters was also confirmed by the observation of weak (111) and (200) peaks by X-ray powder diffraction of the bulk sample.

A film of $[Ag_2(Hfacac)_2(NORPHOS)]_{150}[MTD]_{300}/[MTD]_{200}$ (Ag-2), prepared in a manner analogous to Ag-1 with the same metal content, was found to contain spherical microdomains 280 Å in diameter. After decomposition of the silver complexes in the film under similar conditions, ca. 85 Å clusters were formed within the microdomains, but two clusters were observed within some microdomains.

We conclude that the method described here is useful for synthesizing clusters <100 Å in diameter and are continuing to investigate the scope and limitations of this polymer-based approach to the synthesis of size-selected clusters.

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(13) A calculation based on the density of the $[Ag_2(Hfacac)_2(NORPHOS)]_{150}$ homopolymer (1.56 g/cm^3) gave the following relation: cluster size = 0.31 microdomain size, assuming that the microdomain comprises silver-containing segments only, with very little or no poly(MTD) being present. The density was measured by the flotation method in H_2O/KI solution to which a small amount of soap had been added.

Isolation and Structural Elucidation of a Novel Phosphocysteine Intermediate in the LAR Protein Tyrosine Phosphatase Enzymatic Pathway

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Protein tyrosine phosphatases (PTPases) are of growing importance in understanding the regulation of signal transduction pathways which control hormones and growth factors. Phosphorylation of tyrosyl protein residues is one of the key modes involved in intracellular signaling for selective gene activation. The PTPases are thought to be the counterparts to the protein tyrosine kinases in switching signaling pathways off[1] and on[2-5] by controlling the lifetime of phosphorylated tyrosyl groups. The PTPases are found both in cytoplasmic locations and as a family of transmembrane proteins with intracellular phosphatase domains and extracellular domains presumed to be involved in specific ligand and/or cell–cell interactions. PTPases contain signature motifs including an absolutely conserved and required cysteine residue.

We have overexpressed and purified the catalytic domains of the 200-kDa transmembrane LAR (leukocyte antigen related) PTPase.[6] In addition, the specificity toward several synthetic phosphotyrosyl peptides corresponding to known phosphorylation sites in protein components of cellular signal transduction pathways was determined, and a 40-kDa single-domain fragment, LAR-D1, was shown to retain high catalytic efficiency. We have therefore utilized this representative membrane PTPase fragment for mechanistic studies.[6,7]

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