and 1055 °C resulted in deposition rates of ca. 6.0, 7.0, and 13 μm/h, respectively.

Specular reflectance FTIR of the SiC coatings deposited on Si(100), from DSCB, revealed only one strong absorption at ca. 790–800 cm^{-1}, which is indicative of the Si–C stretch.[15] No adsorption was observed between 1900 and 2200 cm^{-1} or 2800 and 3100 cm^{-1}, which is characteristic of the Si–H and C–H infrared stretching frequencies, respectively.

Powder X-ray diffraction (XRD) was used to determine the relative crystallinity of the coatings. The powder XRD spectra of the coatings deposited from DSCB at 810, 945, and 1055 °C are shown relative to a piece of the "as-received" Si(100) substrate (see Figure 2). The crystallization onset temperature is presumed to be <810 °C, since the β-SiC coating deposited at 810 °C exhibited a relatively intense SiC(111) peak (at a 2θ value of ca. 36°).[16] In comparison, the powder XRD of the SiC films produced in previous studies, from the pyrolysis of I on Si(100), indicated a crystallization onset of >900 °C.[7]

The decomposition onset temperature of II was determined, on Si(100), by using a quadrupole mass spectrometer attached to the LPCVD system, as described previously.[7] The mass peak intensity for H_2(g) ($m/e = 2$), which is the initial decomposition byproduct of II, was monitored as a function of increasing substrate temperature. The results of this experiment indicated that II has a decomposition onset temperature of 680 °C on a Si(100) surface. This decomposition onset temperature of 680 °C for II is ca. 80 °C lower than that previously determined for I (ca. 760 °C)[7] in a similar experiment.

Pyrolysis byproducts produced from the decomposition of II at a maximum Si(100) surface temperature of ca. 850 °C were collected in a series of three liquid N_2 cooled traps for later identification. A minimum of four experiments were performed, at different substrate temperatures, to ensure an ample supply of gases for GCFTIR. The only noncondensable (at 77 K) byproduct detected from II was H_2(g), which is in contrast to both H_2(g) and CH_4(g) detected in previous studies of the pyrolysis of I.[7] Information concerning the pyrolysis chemistry of compound II was obtained by systematically analyzing these trapped byproducts by using the quadrupole mass spectrometer attached to the LPCVD system. The series of cold traps were separately allowed to slowly warm to room temperature while continuously monitoring the m/e peak intensities from 1 to 200 amu. The first series of m/e peaks detected were determined to be a mixture of C_2H_x(g) hydrocarbons followed by a small amount of methylsilane. As the third and final trap approached room temperature, a series of m/e peaks of much greater intensities emerged corresponding to a significant amount of dimethylsilane. These m/e peaks were followed by the final series of mass peaks detected which were attributed to II. In contrast to the results from the previous pyrolysis studies of I,[7] no trimethylsilane or tetramethylsilane was detected. This suggests that the byproducts, from the pyrolysis of II, are not derived from simple recombination of radical species but rather the result of discrete mechanistic decomposition routes, involving H transfer from Si to the adjacent $-(CH_2)-$ group as suggested by previous mechanistic studies.[17,18]

Auger electron spectroscopy (AES) was used to determine the elemental composition of the coatings that were deposited from II at various Si(100) substrate temperatures. The Si and C peak intensities (peak-to-peak heights) were averaged over the SiC(0001) and SiC(000$\bar{1}$) faces of the single-crystal SiC Lely[19] standard, which was used as a reference during each AES determination. The coatings deposited from II at 810 °C contained ca. 2% (atomic) excess silicon, which is consistent with a significant amount of dimethylsilane that was detected from the pyrolysis of II at ≤850 °C. Subsequent coatings deposited at ca. 945 and 1055 °C resulted in stoichiometric silicon carbide. This is in contrast to the AES results of coatings produced using the derivative I of compound II.[7] The films deposited from I in this previous study contained as much as 10% (atomic) excess carbon, as determined by AES.

Further investigations of II, and derivatives thereof, as potential single-source CVD precursors to polycrystalline and single-crystal silicon carbide are currently underway. These investigations include electrical characterization of the films and also a detailed, quantitative evaluation of the pyrolysis byproducts produced as a function of varying both the substrate temperature and substrate material.

Acknowledgment. This work was supported by the Chemistry Division of the Office of Naval Research.

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Synthesis of Silver and Gold Nanoclusters within Microphase-Separated Diblock Copolymers

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Diblock copolymers are known to self-assemble in films to yield microdomains (lamellae, cylinders, or spheres) whose sizes and spacings are typically in the range 100–1000 Å.[1] The geometry of the microdomains and the domain sizes usually can be varied in a predictable manner by adjusting the length of each block and the total molecular weight[2] or by blending with homopolymer.[3] To date, studies largely have concerned purely organic polymers, and the phase behavior of such materials is relatively well-understood. In this communication, we report the

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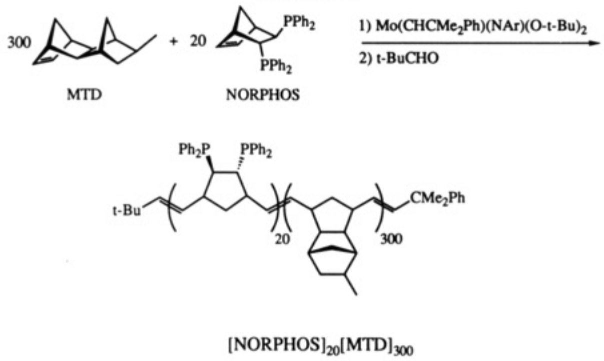
Scheme I



synthesis of diblock copolymers having metal complexes attached selectively to one block, microphase separation in solvent-case films, and decomposition of the confined metal complexes to yield metal nanoclusters.[4] Related studies concerned with the synthesis of semiconductor clusters within microphase-separated materials prepared by ring-opening metathesis polymerization (ROMP) have also appeared recently.[5]

A [NORPHOS]$_{20}$[MTD]$_{300}$[6] diblock copolymer has been synthesized on a 0.5-g scale by adding 300 equiv of MTD followed by 20 equiv of NORPHOS to Mo(CHCMe$_2$Ph)(NAr)(O-t-Bu)$_2$ (Ar = 2,6-C$_6$H$_3$-i-Pr$_2$)[7] as shown in Scheme I. The living polymer is then capped with a neopentylidene group in a Wittig-like reaction with pivaldehyde and isolated quantitatively as an off-white solid by precipitation in pentane. ^{1}H NMR analysis of the block copolymer in C$_6$D$_6$ showed the composition to be that expected (15% by weight of poly-NORPHOS), while gel permeation chromatography yielded a polydispersity index of 1.08 (refractometer and UV detection) with M_n = 81 000 with respect to polystyrene standards (M_n(theory) = 61 500).

Silver and gold were introduced into the polymer in the form of Ag(COD)(Hfacac)[8] or Au(PMe$_3$)Me.[9] One equivalent of metal complex per phosphine was added to the block copolymers in benzene solution, as shown in eqs 1 and 2.

$$[\mathrm{NORPHOS}]_{20}[\mathrm{MTD}]_{300} \xrightarrow[-40\mathrm{COD}]{40\mathrm{Ag(Hfacac)(COD)}} [\mathrm{Ag_2(Hfacac)_2(NORPHOS)}]_{20}[\mathrm{MTD}]_{300} \quad (1)$$

$$[\mathrm{NORPHOS}]_{20}[\mathrm{MTD}]_{300} \xrightarrow[-40\mathrm{PMe_3}]{40\mathrm{Au(PMe_3)(Me)}} [\mathrm{Au_2(Me)_2(NORPHOS)}]_{20}[\mathrm{MTD}]_{300} \quad (2)$$

Solutions that contain approximately 3 wt % polymer (2 equiv of the Ag or Au complexes per NORPHOS) were allowed to evaporate slowly in polyethylene cups in a nitrogen glovebox in the dark over 5–7 days. Silver binds rapidly and quantitatively to triphenylphosphine upon loss of COD;[8] we presume the same is true in the case of poly-NORPHOS. In contrast, although phosphine exchange on gold is fast,[9] binding of gold to NORPHOS is not thermodynamically favored. However, it is driven to completion during film casting as the PMe$_3$ escapes. Films approximately 0.4 mm thick that have been prepared in this manner are hard, transparent, and pale-yellow due to residual Mo(O)(NAr)(O-t-Bu)$_2$.[7] Films that contain silver also have a color that is characteristic of traces of silver clusters (100–500 Å) being present, as

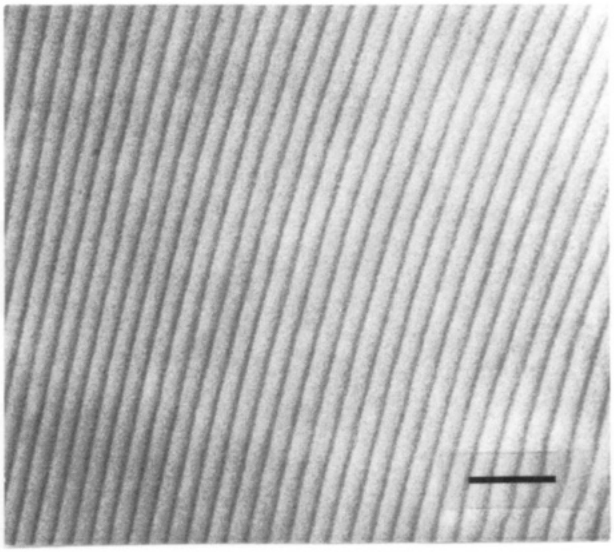


Figure 1. Electron micrograph of Ag-1 (bar = 1000 Å).

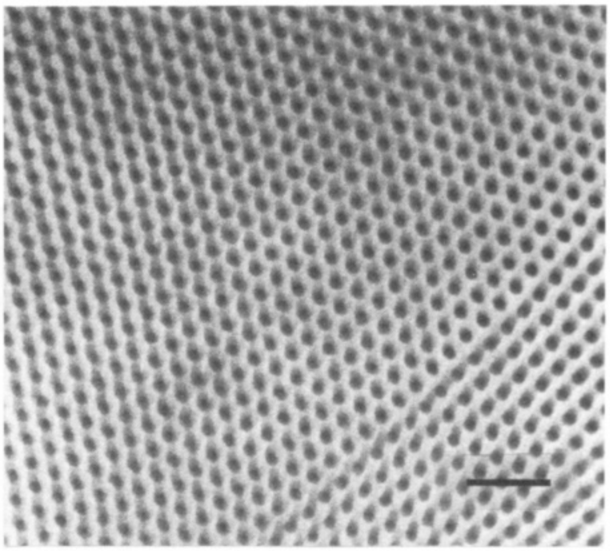


Figure 2. Electron micrograph of Au-1 (bar = 1000 Å).

Table I. Data for Polymers Containing Gold and Silver Complexes Bound to Poly-NORPHOS

polym	M-block,[a] wt %	metal, wt %	morphology[b]
Ag-1	28	5.9	lamellar
Au-1	25	11	cylindrical
Ag-2[c]	20	3.7	cylindrical
Au-2[d]	8.8	3.9	spherical

[a] Refers to the metal-containing block. [b] Observed by TEM. [c] Blend of 70 wt % Ag-1′ with [MTD]$_{50}$.[10] [d] Blend of 34 wt % Au-1 with [MTD]$_{50}$.

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(6) MTD = methyltetracyclododecene (Scheme I), NORPHOS = racemic 2-*exo*-3-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptene (Scheme I), COD = 1,5-cyclooctadiene, and Hfacac = hexafluoroacetylacetonate.

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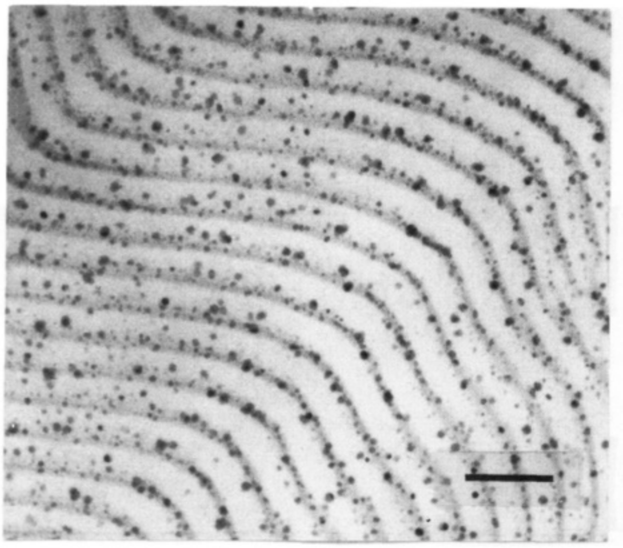

Figure 3. Electron micrograph of Ag-1 after thermal treatment (bar = 1000 Å).

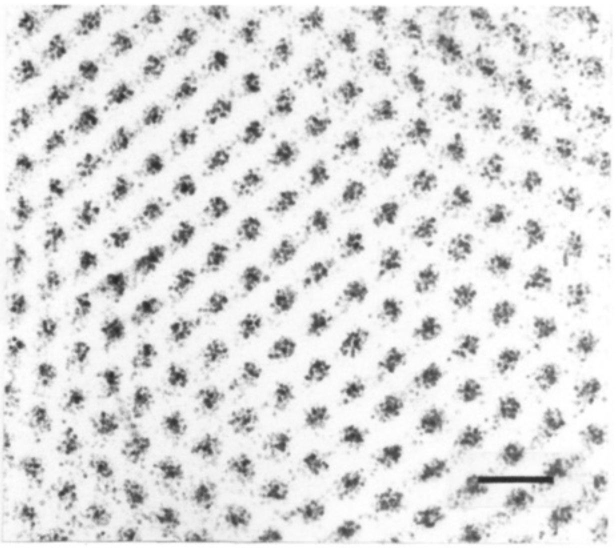

Figure 4. Electron micrograph of Au-1 after thermal treatment (bar = 500 Å).

confirmed by TEM (transmission electron microscopy on a JOEL 200 CX microscope operating at 200 kV). We ascribe the presence of these relatively large clusters to decomposition of unreacted Ag(COD)(Hfacac) during film casting.

A film made from $[Ag_2(Hfacac)_2(NORPHOS)]_{20}$-$[MTD]_{300}$ (Ag-1) exhibits lamellar morphology as shown by TEM of a 200–300-Å thick section (Figure 1). The silver-containing microdomains are about 90 Å thick, and the interdomain spacing is approximately 250 Å. However, a film made from $[Au_2(Me)_2(NORPHOS)]_{20}[MTD]_{300}$ (Au-1) shows cylindrical morphology with a hexagonal packing of the metal-complex-containing cylinders (Figure 2). The diameter of the cylinders is approximately 100 Å and the interdomain spacing approximately 300 Å. In both cases relatively long-range order could be observed. The weight percent of the metal-containing block and weight percent of metal in the polymer film are given in Table I.

Thin sections (200–300 Å) of Ag-1 and Au-1 films were placed on copper grids and heated to 150 °C in air for 15 and 48 h, respectively. The TEM micrographs (Figures 3 and 4) confirm that small clusters have formed which reside largely within the original microdomains. Silver cluster sizes were in the range 20–100 Å, and gold cluster sizes in the range 15–40 Å. Rings ascribable to polycrystalline metal clusters can be observed in both cases by electron diffraction. Some gold migrated to the surface of the film to form large clusters that continued to grow upon prolonged heating of the sample. Heating of *bulk* samples in a Schlenck tube in vacuo or in air also yielded relatively large clusters (>100 Å) that were not confined to the original metal-containing microdomains. The larger clusters were found in higher concentration near the bulk polymer surface. At this stage we are uncertain why relatively large gold clusters near or on the polymer surface form relatively quickly upon heating bulk polymer samples.

Blending of Ag-1′[10] and Au-1 with $[MTD]_{50}$ homopolymer (M_n = 9200, PDI = 1.04) causes a change in microdomain structure (see Table I) as a consequence of the reduced weight fraction of the metal-containing block. The TEM micrographs of these blends (Ag-2 and Au-2, re-

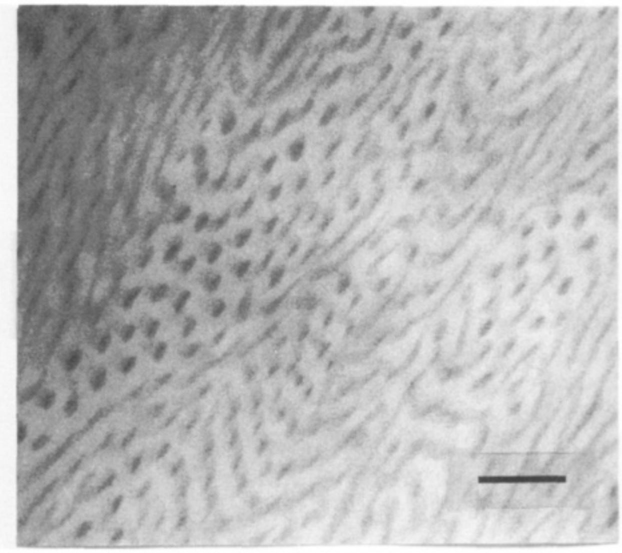

Figure 5. Electron micrograph of Ag-2 (bar = 1000 Å).

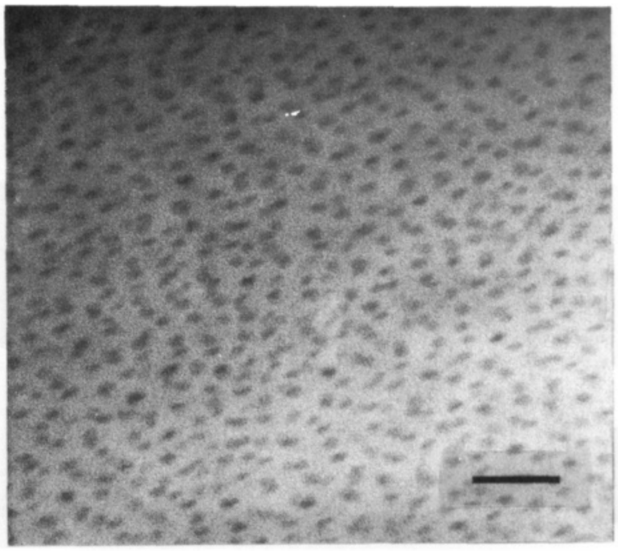

Figure 6. Electron micrograph of Au-2 (bar = 1000 Å).

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[10] Ag-1′ is an independently prepared sample having the composition $[NORPHOS(Ag)_2(Hfacac)_2]_{20}[MTD]_{300}$. After approximately 4 months in air, the sample of $[NORPHOS]_{20}[MTD]_{300}$ that was used to prepare Ag-1′ was shown by GPC (vs polystyrene standards) to have M_n = 63 000 and PDI = 1.10. After 4 months in air, the sample of $[NORPHOS]_{20}[MTD]_{300}$ that was used to prepare Ag-1 was found to have M_n = 72 000 and PDI = 1.2.

spectively) are shown in Figures 5 and 6, respectively. Cylinders with short-range order and disordered spheres[11] were observed in which the metal-containing domain is about 100 Å in diameter.

Further studies are targeted toward understanding the decomposition process and controlling cluster growth in such polymer films. Related studies involving the synthesis of palladium and platinum nanoclusters within microphase-separated diblock copolymers will be reported in full paper format.[12]

Acknowledgment. We thank the National Science Foundation (Grant DMR 87-19217) and Nippon-Zeon for financial support.

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[11] The elongated shape of the spherical microdomains is believed to be caused by shear forces during microtoming.

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Synthesis of ZnS and CdS within ROMP Block Copolymer Microdomains

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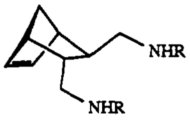
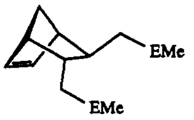
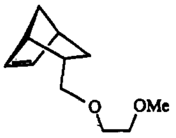
We have initiated a project aimed toward the synthesis of semiconductor clusters of a predictable size within microdomains in films of block copolymers prepared by ring-opening metathesis polymerization (ROMP).[1-3] For example diamide complexes that contain Sn(IV), Sn(II), or Pb(II) have been prepared from diaminonorbornenes (amino NBE, R = *t*-Bu or $SiMe_3$).[2] We report here an approach that involves norbornenes that can bind metals in a dative fashion through sulfur or oxygen donors. This approach allows block copolymers to be prepared and characterized before the metal is attached and, if the binding constant is large enough, for the metal to be added in stoichiometric amounts to the polymer in solution before casting a film and thereby assembling a microphase-separated material. A related approach involving phosphine-derivatized norbornenes has been used to prepare Ag and Au clusters.[4]



amino NBE



7-E (E = O, S)



5-O

Table I. Polymer Specifications

polymer[a]	M_W[b,c]	M_N[b,c]	PDI[c]	MW[d]	%[e]
$(7\text{-O})_{74}(MTD)_{220}$	85	79	1.07	52	26
	86	82	1.04		
$(MTD)_{220}$	62	60	1.02	38	
	61	60	1.02		
$(7\text{-S})_{74}(MTD)_{220}$	66	64	1.03	54	29
	64	63	1.02		31
$(MTD)_{220}$	52	49	1.06	38	
	47	46	1.02		
$(7\text{-S})_{80}(MTD)_{660}$	162	153	1.06	132	13
	159	152	1.05		15
$(7\text{-S})_{80}$	19	18	1.06	17	
	18	17	1.03		
$(5\text{-O})_{80}(MTD)_{220}$	62	59	1.04	53	28
	58	56	1.03		34
$(5\text{-O})_{80}$	20	19	1.06	15	
	19	19	1.03		

[a] Subscripts refer to degree of polymerization. A known quantity of the first block for each diblock was removed for GPC analysis. [b] Values are given with respect to polystyrene standards and should be multiplied by 10^3. [c] Data obtained using a refractometer are listed above those obtained using a UV–vis detector. [d] Molecular weight is calculated on the basis of equivalents employed (multiply by 10^3). [e] Percentages refer to weight ratio of 7-O, 7-S, or 5-O block to diblock; the calculated weight ratio is printed above that obtained by ^1H NMR.

Table II. Binding Constants (M^{-1}; 25 °C, C_6D_6)[a]

	$ZnPh_2$	$Cd[3,5\text{-}C_6H_3(CF_3)_2]_2$
$(7\text{-O})_{100}$[b]	113 (13)	
$(7\text{-S})_{45}$[b]	144 (16)	
7-S		81 (5)
DME[c]	>500	>100

[a] Numbers in parentheses represent 1 standard deviation. [b] Subscript refers to degree of polymerization. [c] 1,2-Dimethoxyethane.

Table III. Percent Complexed Metal

	K (M^{-1})		
$[MR_2]$[a]	100	200	500
0.03	57	67	77
0.06	67	75	83
0.12	75	82	88

[a] $[MR_2]$ refers to total concentration (mol/L) of metal. The calculation assumes an equimolar ratio of binding sites to metal.

Homopolymers of 7-O, 7-S, and 5-O[5] and block copolymers with MTD (methyltetracyclododecene) were prepared employing Mo(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ as the initiator in toluene as described elsewhere.[6,7] All polymerizations were terminated by adding benzaldehyde after the second monomer had been consumed. The polymers were characterized by GPC, ^1H NMR, and (vide infra) TEM. All polydispersities are low (Table I), and ^1H NMR integration confirms that the block-to-block ratio of repeat units is that expected of a well-behaved living polymerization. Homopolymers derived from 7-O, 7-S, and 5-O have T_g values of ca. 45 °C, whereas MTD homopolymer exhibits a T_g of ca. 210 °C.

Binding constants for $ZnPh_2$ binding to $(7\text{-O})_{100}$ and $(7\text{-S})_{45}$ and $Cd[3,5\text{-}C_6H_3(CF_3)_2]_2$ binding to 7-S have been determined by ^1H NMR methods (Table II).[8-10] These data reflect the diminished Lewis acidity of Cd relative to Zn (if we assume that binding to 7-S is approximately

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[5] 7-O was prepared from the diol (see ref 2) via deprotonation (with butyllithium) and methylation (with methyl iodide). 7-S was synthesized from the ditosylate[2] by reaction with $NaSCH_3$. 5-O was obtained by alkylation of the lithium salt of *endo*-2-(hydroxymethyl)norbornene with 2-methoxyethyl bromide. The monomers were characterized by proton and carbon NMR.

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