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.

[12] Ng Cheong Chan, Y.; Craig, G. S. W.; Schrock, R. R.; Cohen, R. E., manuscript in preparation. (b) Presented at the New York ACS meeting, August, 1991; see: *Polym. Prepr.* **1991**, *32*, 128.

Synthesis of ZnS and CdS within ROMP Block Copolymer Microdomains

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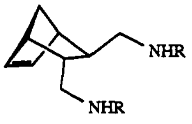
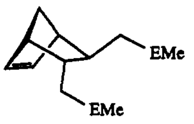
Received November 5, 1991

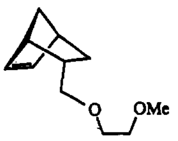
We have initiated a project aimed toward the synthesis of semiconductor clusters of a predictable size within microdomains in films of block copolymers prepared by ring-opening metathesis polymerization (ROMP).[1-3] For example diamide complexes that contain Sn(IV), Sn(II), or Pb(II) have been prepared 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

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.

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.

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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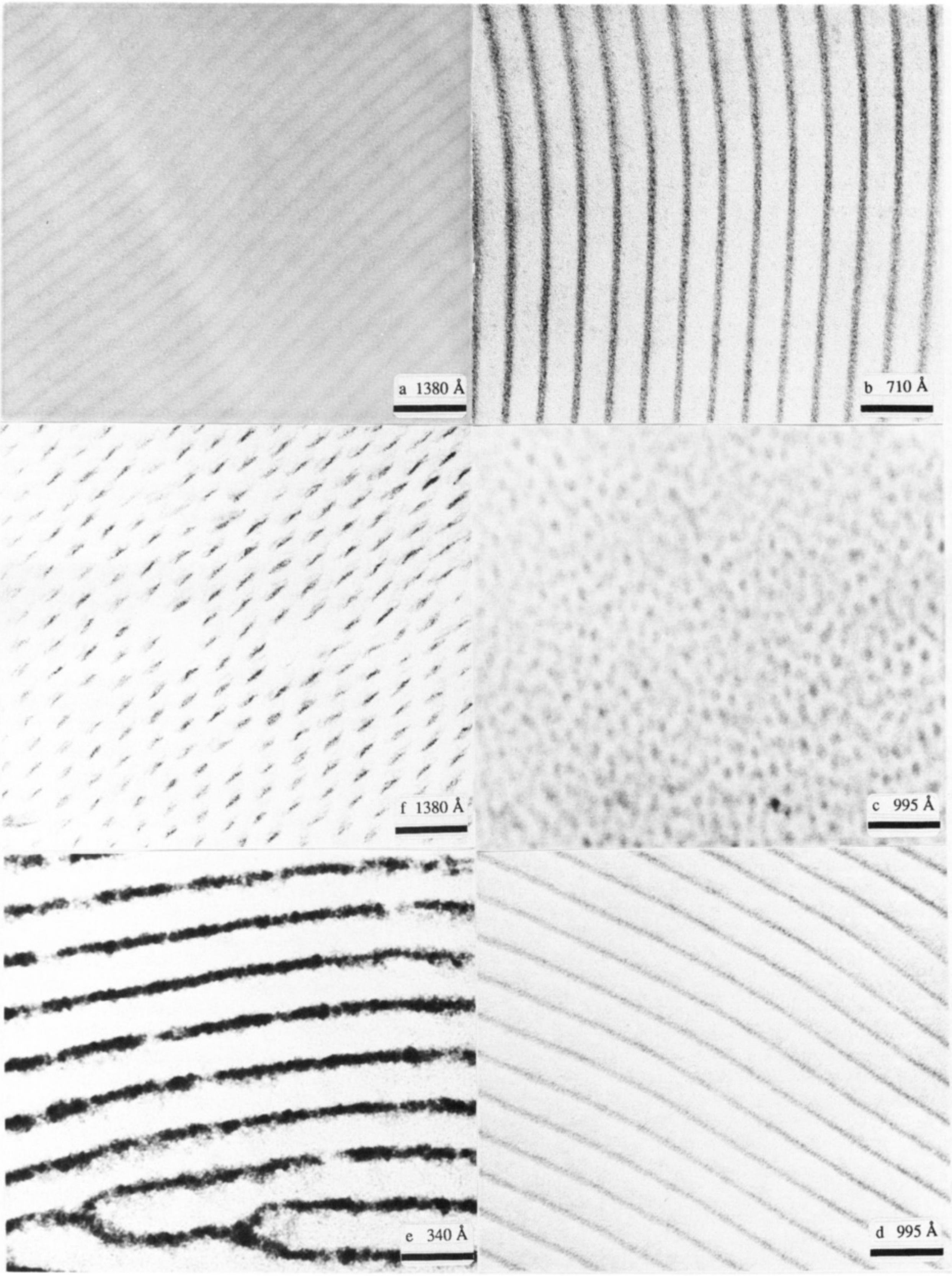

Figure 1. Transmission electron micrographs taken in the bright-field mode on a JEOL 200CX instrument operating at 200-kV accelerating voltage. The individual sample compositions and histories with regard to H_2S-treatment are as follows: (a) (**7-S**)$_{74}$(MTD)$_{220}$, not treated; (b) (**7-S**)$_{74}$(MTD)$_{220}$/74 $ZnPh_2$, 25 °C, 8 h, 1 atm; (c) (**7-S**)$_{80}$(MTD)$_{660}$/80 $ZnPh_2$, 25 °C, 12 h, 1 atm; (d) (**5-O**)$_{80}$(MTD)$_{220}$/80 $ZnPh_2$, 115 °C, 12 h, 1.3 atm; (e) (**5-O**)$_{80}$(MTD)$_{220}$/80 Cd[3,5-$C_6H_3(CF_3)_2]_2$, 115 °C, 12 h, 1.3 atm; (f) (**5-O**)$_{80}$(MTD)$_{220}$/3.1 (MTD)$_{150}$/80 $ZnPh_2$, 195 °C, 66 h, 1.6 atm. After H_2S treatment, samples were ultramicrotomed to give sections ca. 300 Å thick, which were transferred to copper grids for TEM analysis.

the same as binding to ring-opened **7-S**) and the enhanced coordinating ability of S relative to O. An E–M–E (E = O or S) angle of ca. 120° might be anticipated for complexes of **7-E** with MR_2 on the basis of the reported structure of Sn(bTAN)Cl_2,[2] a complex containing a diamidonorbornene ligand derived from amino NBE (R =

t-Bu). Importantly, however, 1,2-dimethoxyethane binds to both Zn and Cd much more strongly than either **7-O** or **7-S**, in accord with what might be expected for a chelating ligand with a small bite angle (approximately 75°[11]), since a small bite angle allows the Zn to maintain a hybridization that is nearly sp.[12–14] Therefore, **5-O** is expected to bind more strongly to Zn and Cd than either **7-O** or **7-S**. Some representative values of percent metal bound as a function of equilibrium constant and concentration can be found in Table III. Since the concentration of metal increases dramatically during the process of casting a film, the metal that is bound should approach 100%.

Figure 1a is a micrograph of a section of a film of $(\mathbf{7\text{-}S})_{74}(\mathrm{MTD})_{220}$ (static cast from benzene). The lamellar morphology can be seen clearly, the contrast being provided by the sulfur in **7-S** (**7-S** block dark, MTD block light). In a separate experiment, 74 equiv of diphenylzinc was added to $(\mathbf{7\text{-}S})_{74}(\mathrm{MTD})_{220}$ dissolved in benzene and a film was then cast. The film was treated with H_2S (see figure captions for conditions) in order to convert the $ZnPh_2$ to $[ZnS]_x$ and benzene.[15–19] Examination by TEM (Figure 1b) revealed the expected lamellar microstructure with interdomain spacings similar to those observed for the film of $(\mathbf{7\text{-}S})_{74}(\mathrm{MTD})_{220}$ alone. X-ray fluorescence in a STEM experiment[20] showed that the ratio of zinc to sulfur in the thinner lamellae (none was observed in the MTD regimes) was 1:3, as expected (two sulfurs per Zn from **7-S**; one sulfur per Zn from H_2S). Figure 1c shows a TEM of a film of $(\mathbf{7\text{-}S})_{80}(\mathrm{MTD})_{660}$ that had been static cast from benzene in the presence of 80 equiv of $ZnPh_2$. The formation of a spherical morphology is consistent with the increased fraction of MTD in the block copolymer. Spherical morphologies may play an important role in the synthesis of essentially monodisperse clusters since the number of metals in the spherical regime can be regulated closely.

Similar results were obtained employing block copolymers containing **5-O**. A well-defined lamellar morphology was observed in a film of $(\mathbf{5\text{-}O})_{80}(\mathrm{MTD})_{220}$ that had been static cast from benzene in the presence of 80 equiv of $ZnPh_2$ (Figure 1d). A film of $(\mathbf{5\text{-}O})_{80}(\mathrm{MTD})_{220}$ that had been static cast from benzene in the presence of $Cd[3,5\text{-}(CF_3)_2C_6H_3]_2$ (Figure 1e) also exhibited this morphology. The latter samples had been treated with H_2S to afford $(ZnS)_x$ and $(CdS)_x$, respectively, within the lamellar microdomains. A cylindrical (wormlike) morphology (Figure 1f) was obtained when a mixture of $(\mathbf{5\text{-}O})_{80}(\mathrm{MTD})_{220}$ and 3.1 equiv of $(\mathrm{MTD})_{150}$ were blended and a film static cast from benzene in the presence of 80 equiv of $ZnPh_2$, consistent with what has been found employing blending techniques in other circumstances.[21]

An important question concerns the nature of the $(MS)_x$ entities formed by reaction of the zinc and cadmium precursors with H_2S within the polymer microdomains. Metal sulfides are readily prepared by this reaction under mild conditions in solution.[15–19] Our data show (e.g., Figure 1) that when the H_2S reaction is conducted at 25 °C, no clusters of appreciable size (>15-Å diameter) are formed. Examination by electron diffraction (selected area diffraction mode on the TEM) of such samples reveals only broad rings in the case of zinc, which are commonly found for amorphous polymers,[22] while some weak, sharper rings

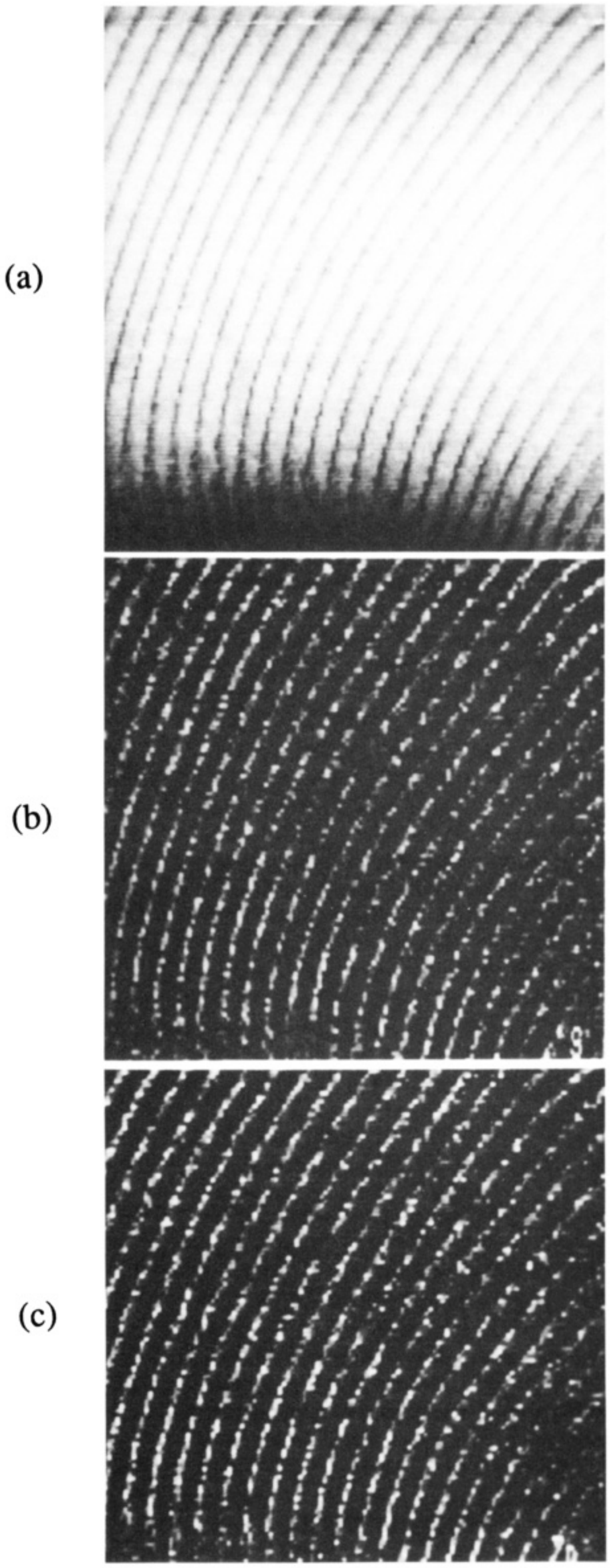

Figure 2. $(\mathbf{5\text{-}O})_{80}(\mathrm{MTD})_{220}/80\ ZnPh_2$ after treatment with H_2S (115 °C, 12 h, 1.3 atm; same as in Figure 1d): (a) bright field image; (b) sulfur X-ray fluorescence map; (c) zinc X-ray fluorescence map.

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are observed in the cadmium case. When the H_2S reaction is carried out at higher temperatures (>100 °C), the electron diffraction patterns sharpen and become more intense for both zinc and cadmium, but any structural assignment would still be tenuous.[23] Since two possible formulations are consistent with a metal-to-sulfur ratio of 1:1, namely $(MS)_x$ and $(RMSH)_x$, it is important to analyze for residual R content, an experiment which was possible for the sample shown in Figure 1e where R = 3,5-$C_6H_3(CF_3)_2$; in this case STEM revealed an approximate ratio of Cd to S of 1:1, and, most importantly, showed that no F was present anywhere in the film. The most reasonable interpretation of these data is that the H_2S reaction produced 2 equiv of volatile 1,3-$C_6H_4(CF_3)_2$ per cadmium. Figure 2 gives X-ray fluorescence maps for S and Zn along with the corresponding bright-field image (same sample as in Figure 1d), showing dramatically that S and Zn (present in a ratio of approximately 1:1) are localized together within the lamellar microdomains.

These experiments illustrate the control that is possible over polymer morphology and demonstrate the selective generation of sulfides of cadmium and zinc within microdomains. Because of the simplicity of this "dative" approach, it may prove to be of wide applicability in semiconductor cluster synthesis, or the synthesis of materials that contain transition metals, if the transition metal can be bound to the donor ligand efficiently.[4] Ultimately, we believe that a spherical microdomain could limit cluster growth to give clusters of a specific size. The controlled methods reported here may offer some advantage over more straightforward methods in which metals have been bound to donors in less well-defined microphase-separated block copolymer (polystyrene/polyvinylpyridine) films.[24]

Acknowledgment. This work has been supported by the National Science Foundation (Grant CHE 9007175). We thank M. Frongillo and Dr. A. J. Garratt-Reed of the CMSE Electron Microscopy Facility at MIT for helpful discussions, and B. F. Goodrich for the gift of MTD. C.C.C. thanks the National Science Foundation for a Graduate Fellowship.

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