Synthesis of PbS Nanoclusters within Microphase-Separated Diblock Copolymer Films

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A lead(II) norbornene derivative, Pb(Cp^N)OTf (Cp^N = 2-(cyclopentadienylmethyl)norborn-5-ene), has been employed along with MTD (MTD = methyltetracyclododecene) to prepare diblock copolymers via ring-opening metathesis polymerization (ROMP). Films of the metal-containing block copolymers that are static cast from benzene contain lead in microphase-separated domains. Treatment of these films with hydrogen sulfide produces nanoclusters of PbS within the microdomains that were characterized by transmission electron microscopy and X-ray powder diffraction. UV-vis absorption spectra of thin films of such materials have a distinct shoulder at ~480 nm.

Introduction

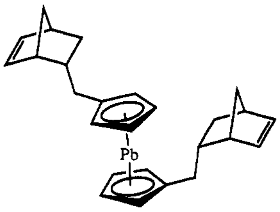
The synthesis of small semiconductor microstructures and microcrystallites ("nanoparticles" or "nanoclusters") is of considerable interest because of the potential exploitation of quantization effects for the preparation of optical signal processors and switches.[1-3] To take maximum advantage of a particular optical property, the nanoclusters ideally should be all the same size. This is the most significant problem associated with nanocluster synthesis. Lead sulfide is one such semiconductor material. Small particles of lead sulfide have been prepared in organic solutions,[4-6] zeolites,[7] glasses,[8] and polymer films,[9-11] and promising third-order NLO properties have been observed.[12,13] The synthesis of kinetically stable semiconductor clusters of controllable sizes in amorphous polymer films is the most desirable in terms of device fabrication. Lead sulfide is a narrow-bandgap semiconductor with an infrared bandgap (0.41 eV) and an ionic crystal structure (cubic rock salt). Lead sulfide also exhibits a high dielectric constant and a large exciton radius. Hence any shift in the absorption threshold with decreasing particle size should be readily observed.

During the past few years we have employed ring-opening metathesis polymerization (ROMP) to prepare nanoparticles within microphase-separated diblock copolymer films.[11,14-19] The initiators for these living polymerizations are well-characterized molybdenum[20] and tungsten[21] alkylidene complexes. The molybdenum complexes appear to be more useful in that they tolerate functionalities to a greater degree than do the tungsten catalysts. This new approach takes advantage of the well-known ability to block copolymers to self-assemble to give lamellae, cylinders, or spheres with dimensions of the order of 50-200Å.[22,23] The nature of the morphology and to some extent the domain size can be altered by varying the amount and ratio of monomer in each copolymer block. The greatest control over particle size and growth is possible in a spherical microdomain; under some circumstances a single metal cluster can be generated in each microdomain.[18,24]

In this paper we report the generation of lead(II) sulfide within microdomains using techniques analogous to those we have used to generate metal clusters within block copolymer films. Experiments that led to the work reported here have been published.[11]

Results and Discussion

In our initial publication[11] we reported the synthesis of block copolymers made from norbornene and the pure *endo* derivative of Pb(Cp^N)$_2$ (eq 2) by ring-opening metathesis polymerization using Mo(CH-*t*-Bu)(N-2,6-C$_6$H$_3$-



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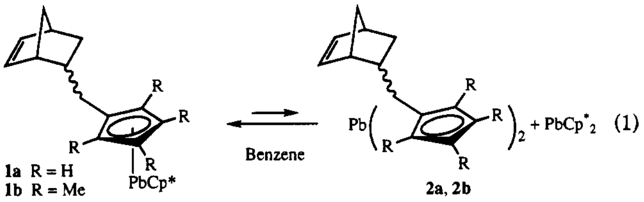
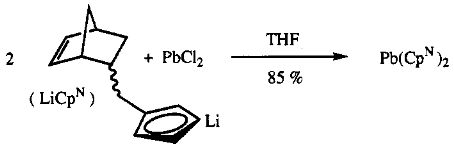
i-Pr$_2$)(O-t-Bu)$_2$ as the initiator. A perceived disadvantage of this approach is the potential for the lead-containing "monomer" to behave as a cross-linking agent. A potential solution was to employ the norbornene derivatives **1a** and **1b** shown in eq 1, which could be prepared from Cp*PbOTf[25] and the lithium salt of the cyclopentadienyl derivative. The lithium salts could be prepared from commercially available 2-hydroxymethylnorborn-5-ene (a mixture of *endo* and *exo* isomers) in a manner analogous to that reported for the pure *endo* derivative when R = H.[26,27] Unfortunately, **1a** and **1b** are not stable in solution toward the redistribution reaction shown in eq 1, a type that is common for other cyclopentadienyl lead complexes;[28] at room temperature the amount of PbCp*$_2$ in equilibrium with **1** in benzene at room temperature was found to be 5–10% for **1a**[27] and >30% for **1b**. Therefore a potential cross-linking agent could still be formed and **1a** and **1b** again would not be ideal for preparing block copolymers in a well-behaved manner whose morphologies would be controlled in the expected manner.

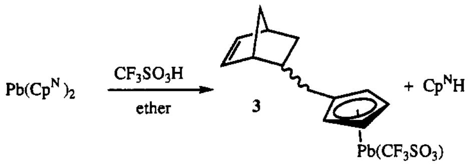


(1)

Bright yellow Pb(Cp^N)$_2$ could be prepared in 85% yield from LiCp^N and PbCl$_2$ (eq 2), the method used to prepare the pure *endo* derivative.[11,27] We were surprised to find that addition of one equivalent of trifluoromethanesulfonic acid in ether to **1** produced Pb(Cp^N)OTf (**3**) as a pale yellow solid quantitatively (eq 3). Unlike the insoluble monocyclopentadienyl monohalide complexes obtained upon treating PbCp$_2$ or PbCp*$_2$ with hydrogen halides,[25,28,29] **3** is very soluble in ether, THF, or benzene, but it is only slightly soluble in pentane. Cp^{N}PbOTf almost certainly forms aggregated structures in the solid state similar to those reported for CpPbBF$_4$ and Cp*PbOTf.[25] The ^{19}F NMR spectrum of **3** in benzene showed only one sharp resonance, while the ^{1}H and ^{19}F NMR spectra in benzene showed no evidence of formation of Pb(Cp^N)$_2$ by a ligand redistribution reaction analogous to that shown in eq 1. Since Cp*PbOTf[25] does not react with Mo(CHCMe$_2$Ph)(NAr)(O-t-Bu)$_2$ (Ar = 2,6-C$_6$H$_3$-i-Pr$_2$)[20,30] over a period of several hours at room temperature, **3** appeared to be suitable for ROMP polymerization. As expected, Cp^{N}PbOTf in benzene solution reacted instantly with H$_2$S to form black PbS.

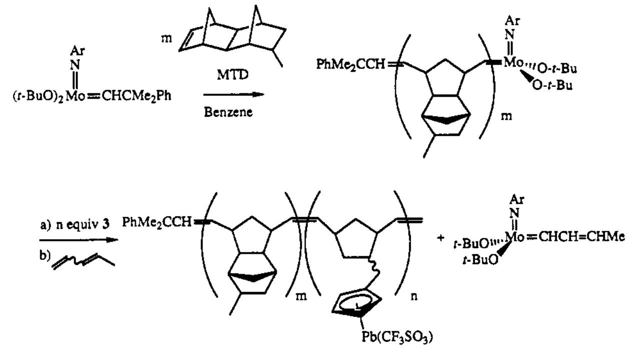


(2)



(3)

Scheme 1



Addition of 5 equiv of Cp^{N}PbOTf to Mo(CHCMe$_2$Ph)(NAr)(O-t-Bu)$_2$ led to rapid formation of a yellow insoluble polymer that could not be characterized. However, block copolymers containing MTD (MTD = methyltetracyclododecene; Scheme 1) as the major monomer proved to be soluble. (MTD was chosen as the comonomer over norbornene since poly(MTD) has a T_g > 200 °C and is readily microtomed. MTD was the comonomer of choice in chemistry in which metal clusters were prepared within block copolymer morphologies.[15,18,24,26]) Block copolymers [MTD]$_m$[Pb]$_n$ (m = equivalents of MTD; n = equivalents of [Cp^{N}PbOTf]) were synthesized on a 700-mg scale by adding m equivalents of MTD to Mo(CHCMe$_2$Ph)(NAr)(O-t-Bu)$_2$ followed (after MTD had been consumed) by n equivalents of **3**, as shown in Scheme 1. The living polymer was capped in a chain-transfer reaction by adding 1,3-pentadiene (a mixture of isomers) to yield a polymer terminated with a methylene group and the vinylalkylidene complex shown.[31] ROMP reactions with this class of initiators are usually terminated by adding benzaldehyde.[19] Benzaldehyde was not employed here since NMR experiments showed that **3** reacted rapidly with benzaldehyde. The PDI (polydispersity index) values of the initial blocks of poly(MTD) (terminated with benzaldehyde) were measured and found to be low, as expected for a living polymerization reaction (Table 1).

Films of these block copolymers were prepared by allowing benzene solutions (~5 mL) to evaporate slowly in polyethylene cups in a nitrogen glovebox over a period of 3–5 days. The films thus obtained were 0.1–0.5 mm thick, flexible, transparent, and yellow to orange in color. In air the films lost their flexibility and color over a period of ~12 h. Upon treatment of the films with H$_2$S under a nitrogen atmosphere at a temperature of 100 °C, they

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Table 1. Polymer Characterization

polymer $[MTD]_m[Pb]_n$							
m	n	% [Pb] (by wt)	PDI of $[MTD]_m$	M_w of $[MTD]_m$[b]	morphology	% PbS (by wt)	domain diameter (Å)[a]
382	3	2.3	1.11	68167	spherical	1.0	20–30
382	5	3.7	1.03	69222	spherical	1.7	20–30
382	20	14	1.03	77135	spherical	6.2	40–50
89	30	50	1.04	31339	wormlike[c]	23	80–133

[a] Average value of several datapoints obtained by TEM. [b] Measured by GPC versus polystyrene standards. [c] Very small PbS clusters are lined up inside tubular microdomains.

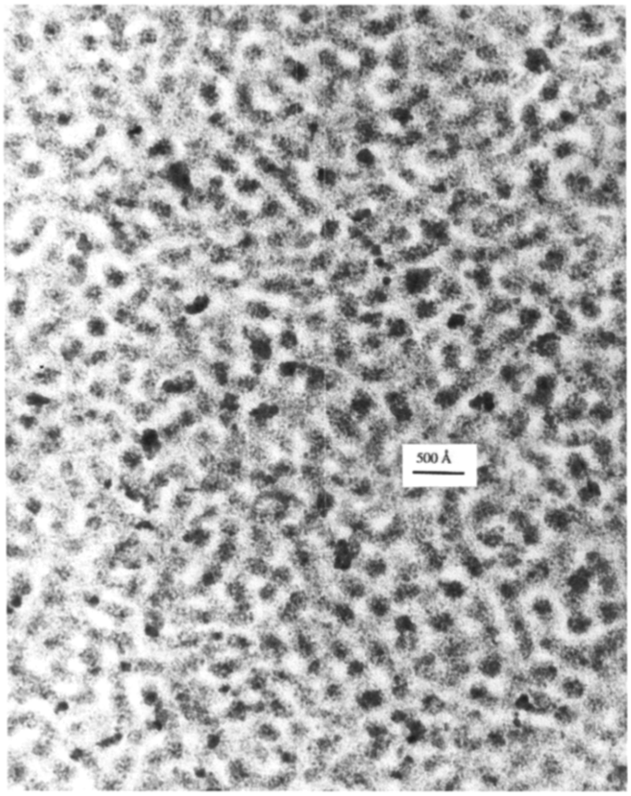

Figure 1. TEM micrograph of $[MTD]_{89}[Pb]_{30}$.

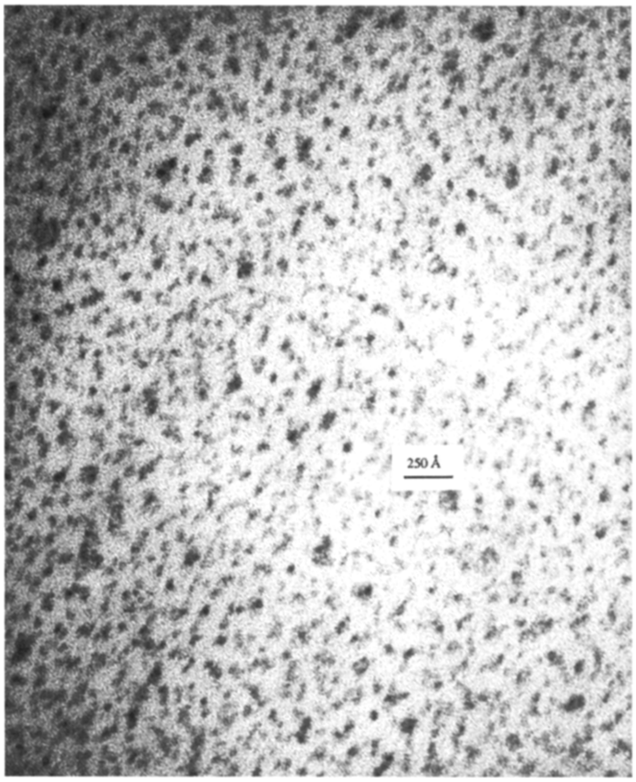

Figure 2. TEM micrograph of $[MTD]_{382}[Pb]_{20}$.

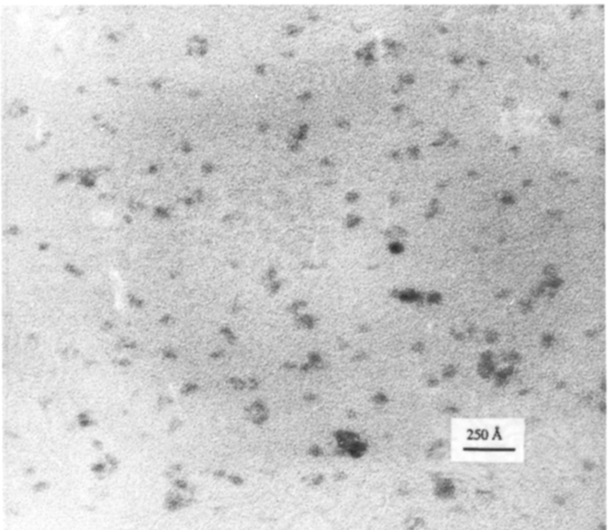

Figure 3. TEM micrograph of $[MTD]_{382}[Pb]_5$.

changed color within 20–30 min to orange, red, or black (depending on the Pb concentration). The samples were kept under H_2S for ~15 h to ensure complete conversion. The UV spectra of films thus obtained remained unchanged over a period of at least 2 months. A $[MTD]_{382}$ homopolymer film prepared and treated in the same manner was essentially transparent beyond 370 nm.

Films exhibited either lamellar/wormlike morphologies (Figure 1), or regular spherical (Figures 2–4) morphologies, depending on the weight percentage of the lead-containing block (Table 1). In the case of $[MTD]_{89}[Pb]_{30}$ a wormlike structure was obtained. A close inspection of the micrograph in Figure 1 reveals that small clusters have formed within each microdomain. A similar wormlike structure was observed for $[Pb(bSAN)]_{20}[MTD]_{176}$ (bSAN = *trans*-2,3-bis[(trimethylsilyl)amidomethyl]norborn-5-ene).[17] In all other samples a spherical morphology was obtained, and several small PbS crystallites were observed within each microdomain. The TEM of $[MTD]_{382}[Pb]_3$ (Figure 4), for example, shows that the PbS clusters range in size from 16 to 25 Å. A potentially important feature of the Cp^NPbOTf approach is the fact that regular spherical morphologies are easily accessible without the need to blend the copolymer with homopolymer. The metal-containing blocks in the block copolymers must readily associate to yield microdomains because of the great disparity in the characteristics of the two blocks; one would not normally expect such a relatively short block to induce microphase separation.[18] This result is most easily explained if one assumes that the Pb-containing regimes of the polymers are forming micellar-like structures in

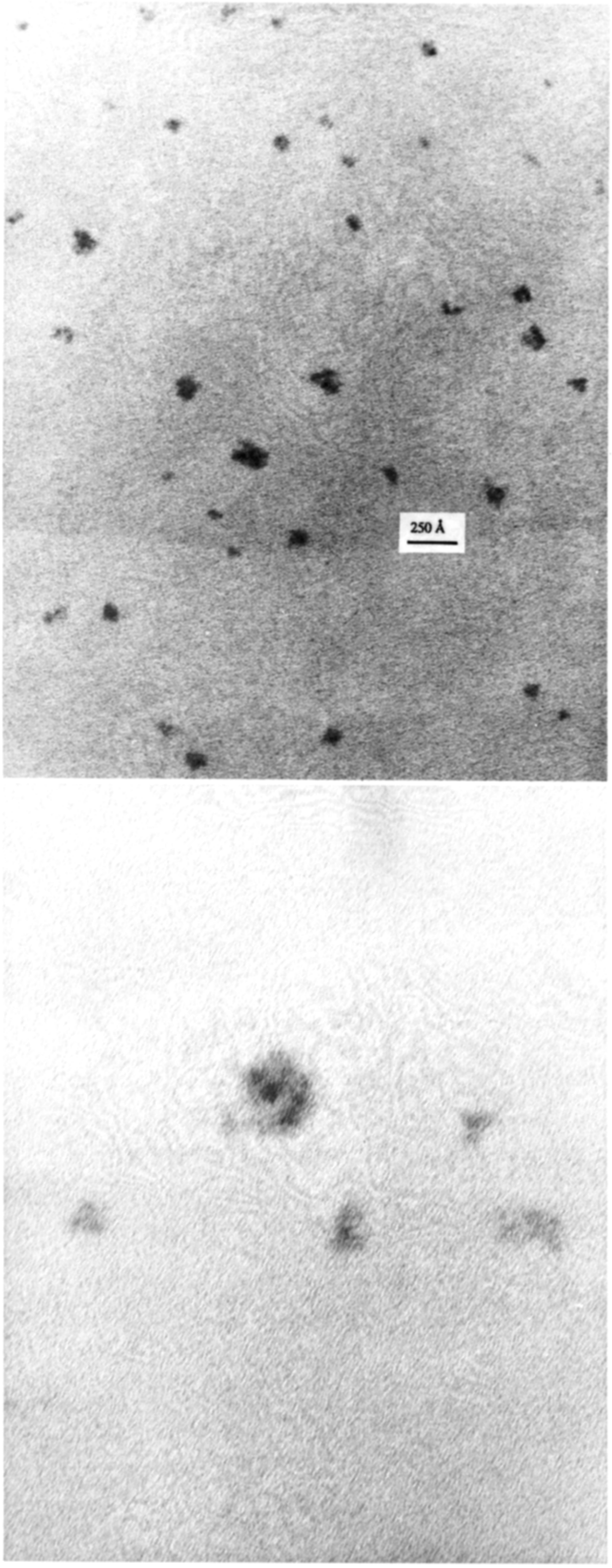

Figure 4. (a, top) TEM micrograph of $[MTD]_{382}[Pb]_3$. (b, bottom) TEM micrograph of $[MTD]_{382}[Pb]_3$.

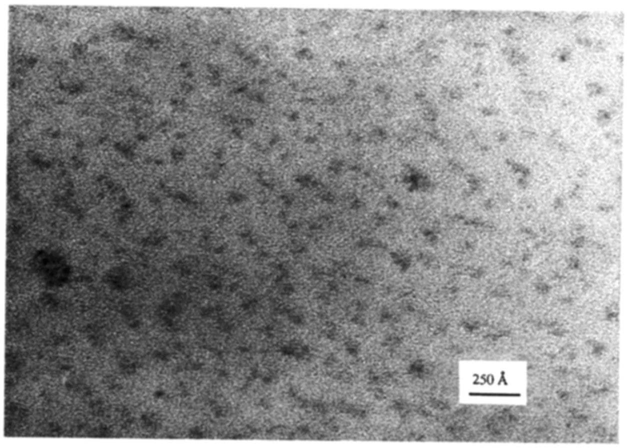

Figure 5. TEM micrograph of "rapidly-prepared" $[MTD]_{382}[Pb]_{20}$.

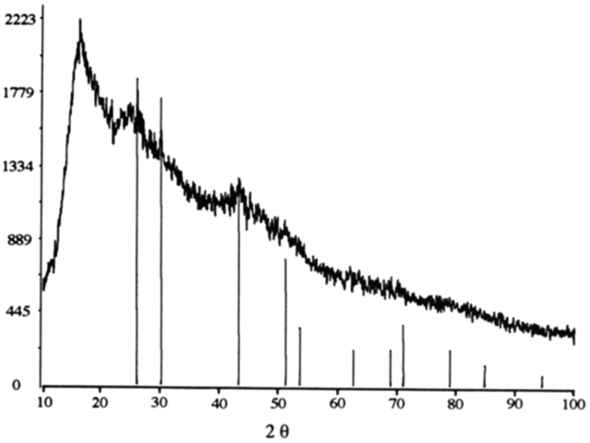

Figure 6. WAXS profile of $[MTD]_{382}][Pb]_{20}$; vertical lines indicate positions of the cubic rocksalt structure of PbS (galena).

solution or during film casting, a phenomenon that perhaps is assisted by aggregation of the cyclopentadienyl lead triflates. In fact, a film prepared by evaporating a benzene solution of $[MTD]_{382}[Pb]_{20}$ in vacuo over a period 1 h was further treated with H_2S to yield a film that contained small regular spheres (Figure 5) similar to those produced in a film that had been slowly cast from solution in the normal manner. The UV–vis absorption spectrum of this "rapidly-prepared" sample (see below) showed the same features as the analogous sample that had been prepared by slow static casting from solution. This finding could have important implications for more rapid and therefore more practical film synthesis.

The X-ray powder diffraction profile of $[MTD]_{382}[Pb]_{20}$ is shown in Figure 6. The vertical lines at the bottom indicate the position of the lines expected for bulk PbS (galena, cubic rock salt structure). Some intensity can be observed for these lines in the polymer matrix. (The strong peak at $2\theta = 16$ is caused by scattering from the amorphous polymer.) The PbS particles are too small to give rise to a sharp diffraction pattern, and therefore no mean particle size could be calculated by using Scherrer's equation. However, the broad bandwidths for the X-ray diffraction lines suggest that the clusters are smaller than 20 Å.[9] Accurate determination of cluster size in $[MTD]_{382}[Pb]_3$ is further hampered by the low concentration of PbS throughout the sample and consequent poor signal-to-noise ratio.

UV–vis absorption spectra of the polymer films containing PbS in spherical microdomains have been examined. An $[MTD]_{382}$ homopolymer film containing traces of residual Mo=CHCH=CHMe complex that had been treated with H_2S is essentially transparent at wavelengths >370 nm. All UV–vis spectra were referenced to this "blank". Typical absorption spectra are shown in Figures 7–9. In all samples absorption begins at ~620–800 nm, wavelengths much shorter than observed for bulk PbS. The onset of absorption was close to what could be expected on the basis of the energy-gap/cluster size relation

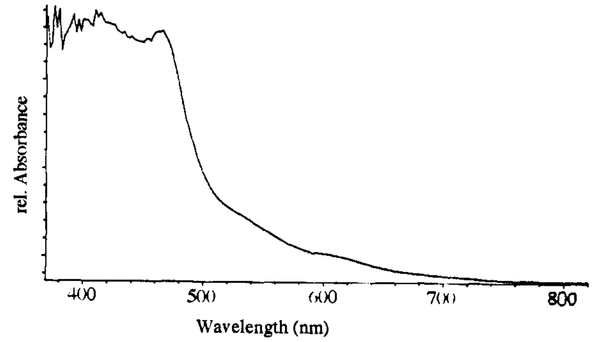

Figure 7. Absorption spectrum of $[MTD]_{82}[Pb]_{30}$.

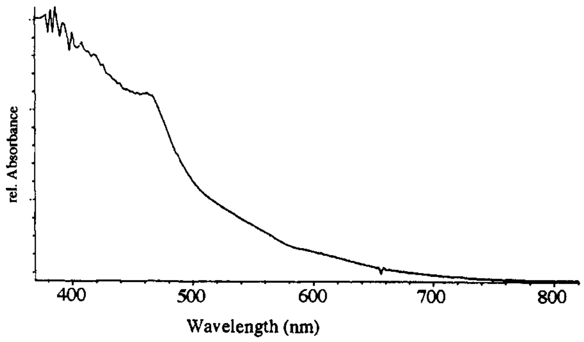

Figure 8. Absorption spectrum of $[MTD]_{382}[Pb]_{10}$.

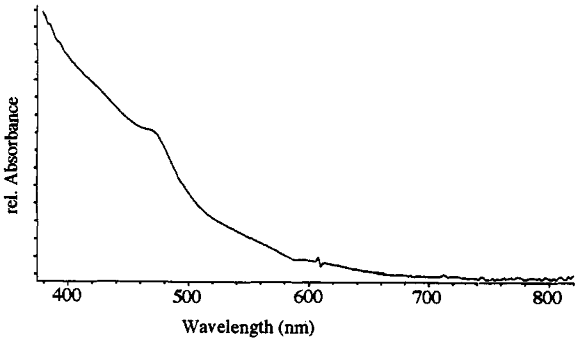

Figure 9. Absorption spectrum of $[MTD]_{382}[Pb]_{5}$ prepared by evaporation of solvent under reduced pressure.

Table 2. UV–Vis Spectra of Lead-Containing Polymers

polymer sample	% PbS in polymer	shoulder (nm)
$[MTD]_{382}[Pb]_{3}$	1.0	480[a]
$[MTD]_{382}[Pb]_{5}$	1.7	480[a]
$[MTD]_{382}[Pb]_{10}$	3.4	475
$[MTD]_{382}[Pb]_{20}$	6.2	475[a]
$[MTD]_{89}[Pb]_{30}$	23	480[a]

[a] Position of absorption peak determined in a second-order derivative spectrum.

described by Wang et al.[9] Most importantly, structure on the absorption edge could be observed in all spectra. Second derivatives of the absorption spectra prove the existence of a discrete shoulder, e.g., at ~480 nm for $[MTD]_{382}[Pb]_{30}$ (Figure 7). The intensity of the shoulder decreases as the amount of PbS in the sample decreases (Figure 8 and 9), but the position of the shoulder did not change significantly with lead sulfide content in the samples we prepared. These findings are summarized in Table 2. In a control experiment 3-equiv of Cp*Pb(OTf) was added to a sample of poly$[MTD]_{382}$, and a film was cast and treated with H_2S in the usual manner. The resulting brittle, black film showed only the characteristic absorption for bulk PbS, no shoulder at ~480 nm. Control experiments mentioned earlier confirm that the shoulder at 480 nm is not present in samples that do not contain PbS.

To observe an exciton maximum in the UV spectrum the size of semiconductor particles should be as uniform as possible. In only a few cases in the literature is a structured UV spectrum for PbS particles reported. A distinct exciton maximum at ~600 nm has been reported for poly(vinyl alcohol)-stabilized PbS colloids which have a particle size of ~30 Å.[4] A value of 476.5 nm has been measured for the transition in laser fluorescence measurements for PbS particles formed in porous glasses.[8] The UV spectrum recorded for molecular PbS in an argon matrix shows a 0–0 transition at 478 nm.[32] Therefore we propose that the transition at ~480 nm in the UV spectra of PbS-containing polymers reported here corresponds to the 0–0 transition in the small clusters (<20 Å) formed within the polymer microdomains.

Experimental Section

General synthetic methods can be found in earlier papers concerned with homo or block copolymer synthesis with initiators of the type employed here.[26,33–35] $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ was prepared as reported in the literature.[20]

Synthesis of $[MTD]_{382}[Pb]_{20}$. A stock solution of 5 mg of $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ in 1 g of benzene was added in one portion to a rapidly-stirred solution of MTD (600 mg, 3.44 mmol) in 6 g of benzene. After 30 min, 2 g of the reaction mixture was removed and 2 drops of benzaldehyde added in order to terminate the polymerization. The polyMTD was precipitated in 100 mL of methanol and dried in vacuo to yield 163 mg of white powder. The PDI was determined by GPC versus polystyrene. To the remaining solution of living polymer was added a solution of 96 mg of Cp^NPbOTf in 2 g of benzene. The mixture was stirred for 1 h, and the polymer was cleaved from the metal by adding 4 drops of 1,3-pentadiene. After 2 h a fraction of the polymer was precipitated in 50 mL of pentane, and the yield of that fraction was employed to estimate the overall yield. The remaining solution was poured into a 5-mL polyethylene vial, and a film was static cast by slowly evaporating the benzene in a drybox over 3–5 days.

A portion of the resulting film was exposed to 1 atm of gaseous H_2S in a closed vessel that was then heated to 100 °C. Within 5–20 minutes the color of the sample became yellow to red. The sample was kept under H_2S for another 12–15 h before microtoming a sample for electron microscopy.

Other samples were prepared similarly. All yields and data are given in Table 1. In all cases the polyMTD portion of the polymer had a low PDI, and estimated yields were greater than 90%.

2-(Tosylatomethyl)norborn-5-ene.[27] Commercially available 2-(hydroxymethyl)norborn-5-ene (17.02 g, 137 mmol; a mixture of endo and exo isomers) was dissolved in 135 mL of pyridine and the mixture was chilled to 0 °C. Tosyl chloride (31.36 g, 164 mmol) was added as a solid in small portions. The reaction was stirred overnight at room temperature and then poured into 600 mL of distilled water. Ether (3 × 100 mL) was added, and the combined organic fractions were dried over $MgSO_4$. The ether solution was filtered and the ether was removed under reduced pressure to yield 13.60 g (80%) of a light yellow oil: ^1H NMR ($CDCl_3$) δ 0.32–0.42 (m, 1, H_{endo}), 1.15 (d, 1, H_7), 1.37 (m, 1, H_7), 1.72 (m, 1, H_{exo}), 2.25 (m, 1, $H_{methine}$), 2.34 (s, 3, Me_{Ar}), 2.71 (br s, 1, bridgehead), 2.81 (br s, 1, bridgehead),

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3.50 (t, 1, CH_2O), 3.75 (m, 1, CH_2O), 5.62 (m, 1, olefin), 6.04 (m, 1, olefin), 7.29 (m, 2, H_{aryl}), 7.72 (m, 2, H_{aryl}).

2-(Cyclopentadienylmethyl)norborn-5-ene.[27] A solution of 2-(tosylatomethyl)norborn-5-ene (12.85 g, 46.11 mmol) in 75 mL of THF was added dropwise at 0 °C to a solution containing NaC_5H_5 (115 mL, 231 mmol, 2.0 M in THF). After the mixture was stirred at room temperature overnight, it was hydrolyzed with saturated aqueous NH_4Cl and extracted with ether. The organic fractions were dried over $MgSO_4$, and the solvent was removed in vacuo. Short-path vacuum distillation of the oily residue (100 °C, 0.5 Torr) afforded 4.92 g (87%) of a colorless oil: ^1H NMR ($CDCl_3$) δ 0.58 (m, 1, H_{endo}), 1.23 (d, 1, H_7), 1.38 (m, 1, H_7), 1.86 (m, 1, H_{exo}), 2.13 (m, 1, Cp), 2.27 (m, 1, Cp), 2.40–2.55 (m, 1, $H_{methine}$), 2.74 (br s, 1, bridgehead), 2.90 (br s, 1, bridgehead), 5.97–6.25 (m, 4, Cp), 6.40 (m, 2, olefin).

2-[(Cyclopentadienyllithium)methyl]norborn-5-ene.[27] Cp^NH (4.92 g, 0.029 mol) was dissolved in 100 mL of cold pentane, and 11.6 mL of BuLi (0.030 mol, 2.5 M in hexane) was added via syringe. After a few minutes the white product began to precipitate. After 3 h the reaction flask was chilled to −40 °C. After 12 h the white product was collected by filtration and dried in vacuo; yield 4.63 g (88%).

$Pb(Cp^N)_2$.[27] $PbCl_2$ (546 mg, 1.96 mmol) was added to a stirred slurry of $LiCp^N$ (700 mg, 2.86 mmol) in 20 mL of THF. After 3 h the solvent was evaporated in vacuo. The resulting bright yellow solid was extracted with 20 mL of pentane, and the extract was filtered through a bed of Celite. The pentane solution was removed in vacuo, and the residue was recrystallized from a minimum amount of ether of yield 916 mg (85%) of yellow product: ^1H NMR (C_6D_6) δ 0.64 (ddd, 1, H_{endo}), 1.16 (d, 1, H_7), 1.50 (m, 1, H_7), 1.80 (ddd, 1, H_{exo}), 2.18 (m, 1, $H_{methine}$), 2.35 (m, 2, Cp), 2.78 (br s, 1, bridgehead), 2.69 (br s, 1, bridgehead), 5.69–5.84 (m, 4, Cp), 6.03 (m, 1, olefin), 6.13 (m, 1, olefin); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 33.35 (CH_2), 34.47 (CH_2), 42.57 (bridgehead), 43.33 (CH), 46.48 (bridgehead), 50.05 (C_7), 109.45 (Cp), 109.71 (Cp), 111.05 (Cp), 111.34 (Cp), 130.65 (Cp), 132.81 (olefin), 137.37 (olefin). Anal. Calcd for $C_{26}H_{30}Pb$: C, 56.81; H, 5.50. Found: C, 56.51; H, 5.55.

Cp^NPbOTf. A solution of triflic acid (TfOH, 212 mg, 1.42 mmol) in 5 mL of ether was added dropwise to a cold (−40 °C) solution of $Pb(Cp^N)_2$ (780 mg, 1.42 mmol) in 30 mL of ether; the color changed from bright yellow to dull yellow during this period. After the reaction was stirred mixture overnight, the solvent was removed under reduced pressure, and the yellow residue was rinsed with cold pentane. Recrystallization of the resulting solid from ether afforded 710 mg (95%) of light yellow product: ^1H NMR (C_6D_6) δ 0.50 (m, 1, H_{endo}), 1.46 (d, 1, H_7), 1.49 (d, 1, H_7), 1.76 (dt, 1, H_{exo}), 2.07 (m, 1, methine), 2.36 (m, 2, Cp), 2.68 (br s, 1, bridgehead), 5.92 (m, 2, Cp), 5.97 (m, 3, Cp and olefin), 6.11 (m, 1, olefin); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 32.73 (CH_2), 33.12 (CH_2), 41.95 (bridgehead), 43.13 (CH), 46.14 (bridgehead), 49.81 (C_7), 110.36 (Cp), 112.08 (Cp), 132.45 (olefin), 133.85 (Cp), 137.26 (CF_3), 137.66 (olefin); ^{19}F NMR (C_6D_6) δ −82.55 (s); IR cm^{-1} 1019 (OTf), 627 (OTf). Anal. Calcd for $C_{14}H_{15}SO_3F_3Pb$: C, 31.88; H, 2.87; Found: C, 31.58; H, 2.93.

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