# Synthesis of PbS Nanoclusters within Block Copolymer Nanoreactors

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Received February 1, 1996. Revised Manuscript Received April 9, 1996<sup>®</sup>

We have demonstrated the synthesis of PbS nanoclusters within the microphase-separated films of diblock copolymers containing carboxylic acid units on one of the blocks. Lead was selectively sequestered into the acid containing domains by treating the polymer films with tetraethyllead, and PbS was formed by subsequently treating the films with H<sub>2</sub>S. The PbS nanoclusters were characterized by X-ray diffraction, X-ray fluorescence, electron microscopy, and UV-vis spectroscopy. The cluster size could be controlled by varying processing parameters such as temperature, the presence of coordinating bases, and the  $H_2S$  exposure time. Increasing the size of the nanoreactors increased the cluster size. The universal cluster synthesis scheme enabled multiple passes through the process, which were used to increase the cluster size and which could in principle be used to passivate the surface of the PbS cluster or to produce mixed semiconductor clusters.

#### Introduction

Semiconductor nanoclusters, i.e., particles with diameters between 1 and 10 nm,<sup>1</sup> have been the subject of numerous investigations in the past few years.<sup>2–13</sup> Lead sulfide nanoclusters are the focus of this work. Lead sulfide, because of its small effective mass, shows a large blue-shift in its absorption edge with a small change in cluster size. Several attempts have been made to quantitatively predict such shifts for various semiconductor clusters, 2-5 including one recent study by us for the particular case of lead sulfide.<sup>14</sup> Bulk lead sulfide has an infrared bandgap (0.41 eV),<sup>15</sup> which shifts to the visible region for the nanoclusters. As a result, lead sulfide nanoclusters may find use in electroluminescent devices such as light-emitting diodes. In addition, lead sulfide nanoclusters are expected to have exceptional third-order nonlinear optical properties,<sup>16</sup> and may also be useful in optical devices such as optical

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- Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
   Lippens, P. E.; Lannoo, M. *Phys. Rev. B* **1989**, *39*, 935.
   Lippens, P. E.; Lannoo, M. *Phys. Rev. B* **1990**, *41*, 6079.
- (4) Rama Krishna, M. V.; Friesner, R. A. J. Chem. Phys. 1991, 95, 8309
- (5) Hill, N. A.; Whaley, K. B. J. Chem. Phys. 1993, 99, 3707.
- (6) Fischer, Ch.-H.; Weller, H.; Katsikas, L.; Henglein, A. Langmuir 1989, 5, 429.
- (7) Eychmuller, A.; Katsikas, L.; Weller, H. Langmuir 1990, 6, 1605. (8) Schooss, D.; Mews, A.; Eychmuller, A.; Weller, H. Phys. Rev. B 1994, 49, 17072.
- (9) Wang, Y.; Herron, N.; Caspar, J. Mater. Sci. Eng. 1993, B19, 61
- (10) Bawendi, M. G.; Kortan, A. R.; Steigerwald, M. L.; Brus, L. E. J. Chem. Phys. 1989, 91, 7282
- (11) Bawendi, M. G.; Carroll, P. J.; Wilson, W. L.; Brus, L. E. J.
- (11) Bawendi, M. G., Carton, T. S., Wilson, M. E., Draz, Z. Z. C. *Chem. Phys.* **1992**, *96*, 946.
  (12) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
  (13) Dabbousi, B. O.; Murray, C. B; Rubner, M. F.; Bawendi, M. G.
- Chem. Mater. 1994, 6, 216.
- (14) Kane, R. S.; Cohen, R. E.; Silbey, R. J. Phys. Chem., 1996, 100, 7928
- (15) Wang, Y.; Suna, A.; Mahler, W.; Kasowski, R. J. Chem. Phys. 1987, 87, 7315.
  (16) Wang, Y. Acc. Chem. Res. 1991, 24, 133.

switches. Lead sulfide nanoclusters have been synthesized in polymers<sup>15</sup> and in zeolites.<sup>17</sup> Functionalized monolayers at water-air interfaces have been used to generate lead sulfide particulate films.<sup>18,19</sup> Rossetti et al.<sup>20</sup> and Nozik et al.<sup>21</sup> have reported quantum size effects seen in PbS colloidal solutions. Other properties have also been studied: Mukherjee et al.<sup>22</sup> have studied the electrical resistivity of nanocrystalline PbS grown in polymer films, and Kyprianidou-Leodidou et al.<sup>23</sup> have studied the effect of PbS colloidal particles on the refractive index of nanocomposites. We have been working on the synthesis of semiconductor nanoclusters with controllable sizes and narrow size distributions within processible block copolymer matrixes prepared via ring-opening metathesis polymerization (ROMP). Previously, semiconductor clusters were synthesized within microphase-separated diblock copolymer films by a scheme in which metal complexes were attached to one block of the copolymer before microdomain formation.<sup>24-26</sup> Sankaran et al.<sup>27</sup> and Tassoni et al.<sup>28</sup> have used this approach to make PbS nanoclusters, using lead-containing norbornene derivatives as one

- (18) Yuan, Y.; Cabasso, I.; Fendler, J. H. Chem. Mater. 1990, 2, 226.
- New York, 1994; Vol. 113.
- (20) Rossetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. J. Phys. Chem. 1985, 89, 1406.
- (21) Nozik, A. J.; Williams, F.; Nenadovic, M. T.; Rajh, T.; Micic, O. I. J. Phys. Chem. 1985, 89, 397. (22) Mukherjee, M.; Datta, A.; Chakravorty, D. Appl. Phys. Lett.
- 1994, 64, 1159. (23) Kyprianidou-Leodidou, T.; Caseri, W.; Suter, U. W. J. Phys.
- Chem. 1994, 98, 8992. (24) Cummins, C. C.; Schrock, R. R.; Cohen, R. E. Chem. Mater.
- 1992, 4, 27. (25) Yue, J.; Sankaran, V.; Cohen, R. E.; Schrock, R. R. J. Am.
- (26) Tuc, 9., 22115, 4409.
  (26) Sankaran, V.; Yue, J.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J. Chem. Mater. 1993, 5, 1133.
- (27) Sankaran, V.; Cummins, C. C.; Schrock, R. R.; Cohen, R. E.; (28) Tassoni, R.; Schrock, R. R. Chem. Mater. 1994, 6, 744.

S0897-4756(96)00072-5 CCC: \$12.00 © 1996 American Chemical Society

(19) Fendler, J. H. Advances in Polymer Science; Springer-Verlag:

<sup>&</sup>lt;sup>‡</sup> Department of Chemistry.

<sup>&</sup>lt;sup>®</sup> Abstract published in Advance ACS Abstracts, July 15, 1996.

<sup>(17)</sup> Wang, Y.; Herron, N. J. Phys. Chem. 1987, 91, 257.

Scheme 1. Yue et Al.'s Universal Nanocluster Synthesis Scheme



block of the diblock copolymer.

A new approach has been developed by Yue et al.,<sup>29</sup> which is illustrated in Scheme 1. The technique involves the selective sequestering of metals into the preformed microdomains of a block copolymer film. Metals can be loaded from solutions of metal salts or by permeation of an organometallic compound. Once loaded, these metal-containing domains serve as localized reaction sites for cluster synthesis, for example, via reaction with H<sub>2</sub>S to form metal sulfides. The spatially distinct domains can be thought of as nanoreactors within which nanoclusters are synthesized. This method can be viewed as a solid-state version of the locus control concept used by Smith and Cheatham<sup>30</sup> to generate colloidal dispersions of selenium in dilute polymer solutions. One advantage of this method is that treatment with H<sub>2</sub>S regenerates the carboxylic acid reactive sites. The loading cycle can therefore be repeated to produce larger clusters. The loading cycle can also be repeated with a different metal, to produce mixed clusters with potentially novel properties. We have used the method of Yue et al.<sup>29</sup> to synthesize PbS nanoclusters.

#### **Experimental Section**

**Chemicals and Reagents.** Anhydrous toluene (99.8%) was purchased from Aldrich. Prior to use, it was stirred over sodium for 12 h and filtered through a sintered glass frit. The ROMP initiator Mo(CHCMe<sub>2</sub>Ph)(NAr)(o-*t*-Bu)<sub>2</sub> (Ar = 2,6-diisopropylphenyl) was purchased from Strem. Methyltetra-cylododecene (MTD) donated by B.F. Goodrich was vacuum distilled, degassed, and stored over sodium, prior to use. The monomer 2-norbornene-5,6-dicarboxylic acid (NORCOOH) was synthesized by the Diels-Alder reaction between cyclopenta-diene and fumaric acid.<sup>31</sup> Hydrogen sulfide (H<sub>2</sub>S), C.P. grade, was purchased from Matheson. Tetraethyllead was purchased from Aldrich.

Scheme 2. Synthesis of MTD/NORCOOH Diblock Copolymer by ROMP



**Polymerization.** All polymerizations were carried out inside a Vacuum Atmospheres nitrogen glovebox. The diblock copolymer used in this study was  $(MTD)_x(NORCOOH)_y$ , where *x* and *y* represent the number of equivalents of monomer used per equivalent of the initiator. As shown in Scheme 2, the block copolymer was synthesized by the sequential addition of the monomers to the initiator Mo(CHCMe<sub>2</sub>Ph)(NAr)(*o*-*t*-Bu)<sub>2</sub> in toluene by adding *x* equiv of MTD followed by *y* equiv of 2-norbornene-5,6 dicarboxylic acid bistrimethylsilyl ester (NOR-COOTMS).<sup>31</sup> The polymerization was terminated by the addition of benzaldehyde.

As an example, the synthesis procedure for a (MTD)<sub>800</sub>/ (NORCOOH)<sub>30</sub> diblock copolymer is described below. The initiator solution (77.58  $\mu$ L) in toluene (0.031 g/mL) were added to a stirred solution containing 0.6 g of MTD in 15 mL of toluene. After 15 min, 150  $\mu$ L of the reaction mixture were withdrawn, diluted with 2 mL of toluene, and terminated by adding an excess of benzaldehyde. This aliquot was used to obtain the molecular weight of the poly(MTD) by the use of gel permeation chromatography. A solution of 42 mg of NORCOOTMS in 2 mL of toluene was then added to the reaction mixture. After 45 min, 10  $\mu L$  of benzaldehyde was added to terminate the polymerization. The solution was stirred for another 45 min to ensure complete termination. The conversion of the (NORCOOTMS)<sub>v</sub> to (NORCOOH)<sub>v</sub> was effected by hydrolysis of the reaction mixture. The copolymer was then precipitated from 300 mL of stirred pentane, collected by vacuum filtration, and washed with excess pentane to remove the molybdenum initiator.

<sup>(29)</sup> Yue, J.; Cohen, R. E. Supramol. Sci. 1994, 1, 117.

<sup>(30)</sup> Smith, T. W.; Cheatham, R. A. *Macromolecules* **1980**, *13*, 1203. (31) Saunders, R. S. Ph.D. Thesis, Massachusetts Institute of Technology, 1992.

Table 1. Block Copolymer Compositions and Morphologies

<b>F8</b>		
sample	MTD/COOH	morphology
Α	500/20	wormlike
В	500/20	spherical
С	800/30	spherical

The purified polymer was dried under vacuum for 24 h. The dried polymer was redissolved in THF, and the solution was transferred to a Teflon cup inside a glass jar. The THF was allowed to evaporate slowly over 5-7 days to obtain a transparent polymer film, which was further dried under vacuum for 24 h.

**Tetraethyllead Treatment.** The polymer film was covered with drops of tetraethyllead and allowed to react for 12 h. The unreacted tetraethyllead was removed under vacuum, and the polymer film was subsequently heated under vacuum at 150 °C for 1 h.

**Hydrogen Sulfide Treatment.** The tetraethyllead-treated polymer films were sealed in a glass bomb reactor equipped with a Teflon stopcock. The bomb reactor was evacuated prior to  $H_2S$  treatment.

Room-Temperature Reaction. The evacuated bomb reactor was refilled with C.P. grade  $H_2S$ , and the reaction was allowed to continue for 15 h. The amount of  $H_2S$  gas added was controlled by setting the cylinder pressure gauge to 15 psig and allowing the gas to fill the reactor for 10 s. After 15 h, the bomb reactor was opened in the fume hood, and the excess  $H_2S$  gas was allowed to dissipate over 6-8 h. The polymer film was further pumped under vacuum to remove residual  $H_2S$ .

High-Temperature Reaction. The evacuated bomb reactor was heated to the desired temperature in an oil bath for an hour. The bomb reactor was then filled with  $H_2S$  as described above. The reaction was allowed to proceed for 15 h, after which the reactor was cooled to room temperature, and the excess  $H_2S$  gas was dissipated. The polymer film was further pumped under vacuum to remove residual  $H_2S$ .

Reaction in the Presence of Pyridine. The polymer films were suspended over 2 mL of pyridine, the reactor was partially evacuated, and the films were allowed to soak in the solvent vapors for 12 h. The  $H_2S$  reaction was then carried out in a manner identical with that for the room temperature reaction.

**Morphological Studies.** *WAXD.* All X-ray data were collected for bulk samples using a Rigaku instrument with a 1.54 Å Cu K $\alpha$  rotating-anode point source. The source was operated at 50 kV and 60 mA, and the K $\beta$  radiation was eliminated using a nickel filter. The diffractometer and the goniometer attachment were controlled using the DMAXB Rigaku software. All X-ray diffraction data were collected in reflection mode with a step size of 0.05°.

*TEM.* Ultrathin sections (~40 nm thick) for microscopic studies were prepared by sectioning films with an LKB Ultratome II (Model 8800) and depositing them on gold grids. Transmission electron microscopy experiments were performed on a JEOL CX-200 instrument, with an operating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) was done on an Akashi EM-002B microscope operating at 200 kV. X-ray fluorescence was performed on a VG-HB5 scanning transmission electron microscope (STEM) at an operating voltage of 100 kV.

**UV–Vis Spectroscopy.** Optical spectra of bulk films were obtained on a Cary 5E UV–vis-NIR spectrophotometer using illumination from a tungsten halide lamp. All data were collected with a selected bandwidth of 3 nm, a step size of 1 nm, and a collection time of 1 s/step.

## **Results and Discussion**

**General Information Concerning Polymers.** Polymers were synthesized by ROMP, as discussed in the Experimental Section. Their composition and morphological characteristics are summarized in Table 1.

Polymers A and B had different morphologies, although they had the same target composition. This is a result of the kinetic barriers<sup>32</sup> to attainment of the equilibrium phase-separated morphology, and the faster evaporation of the solvent while static casting films of polymer A. The morphologies were determined by transmission electron microscopy (TEM). The (MTD)<sub>*x*</sub>(NORCOOH)<sub>*y*</sub> diblock copolymers had insufficient contrast to image the morphology directly. The acid-containing domains could however be selectively stained by treating the polymer films with diethylzinc or with tetraethyllead. Loading of metals within the microphase-separated domains enables visualization of these domains by TEM.

**Loading the Nanoreactors with Lead.** As shown in Scheme 1, the first step in cluster synthesis involves loading the nanoreactors with the metal of interest (lead). Proper choice of the lead-containing reagent is crucial. Loading can be attempted from aqueous solutions of lead salts such as lead chloride or lead acetate. The loading of bulk polymer films is diffusion-limited, and it can take a couple of weeks to load metals from solution. Since much faster loading takes place using organometallic reagents, tetraethyllead was chosen as the reagent for loading lead.

Organometallic reagents such as dimethylcadmium, and diethylzinc have previously been used by Yue et al.<sup>29</sup> to load diblock copolymer nanoreactors. Loading of lead is more complicated, because lead is tetravalent in its organometallic compounds and divalent in its inorganic compounds. The desired product after treatment of the polymer films with tetraethyllead is the lead dicarboxylate, which will react with H<sub>2</sub>S to give lead sulfide. Our experimental protocol for tetraethyllead treatment was developed by considering the reaction of tetraethyllead with acetic acid.<sup>33,34</sup> Robinson has shown<sup>34</sup> that tetraethyllead reacts with acetic acid slowly at room temperature forming triethyllead acetate, and that at elevated temperatures complete decomposition to lead(II) acetate occurs. Lead loading in our nanoreactors is analogously accomplished by treating the polymer films with tetraethyllead at room temperature for 12 h, removing the unreacted tetraethyllead, and heating the polymer films under vacuum at 150 °C for an hour.

**Formation of PbS Nanoclusters.** When the tetraethyllead-treated polymer films are exposed to  $H_2S$  gas, the transparent polymer films turn yellow within a minute and eventually turn orange. The formation of lead sulfide clusters was confirmed by X-ray diffraction and by X-ray fluorescence spectroscopy which indicated the presence of Pb and S atoms within the microphase-separated acid domains. The size of these lead sulfide nanoclusters is an important parameter which determines the bandgap and consequently optical properties such as the absorption spectrum. Several processing parameters were used to vary the size of the PbS clusters produced within the diblock copolymer nanoreactors.

Multiple loading. As shown in Scheme 1, treatment with  $H_2S$  regenerates the reactive carboxylic acid units. The nanoreactors can therefore be reloaded with lead,

<sup>(32)</sup> Cohen, R. E.; Bates, F. S. *J. Polym. Scie. Polym. Phys. Ed.* **1980**, *18*, 2143.

<sup>(33)</sup> Shapiro, H.; Frey, F. W. *The Organic Compounds of Lead*, John Wiley & Sons: New York, 1968.
(34) Robinson, G. C. *J. Org. Chem.* 1963, *28*, 843.



**Figure 1.** Representative micrographs of the  $(MTD)_{800}$ -(NORCOOH)<sub>30</sub> diblock copolymer after PbS nanocluster formation: (a) 1 loading; (b) 2 loadings.

and the  $H_2S$  reaction can be repeated to produce larger PbS nanoclusters. Electron micrographs for PbS formation in films of  $(MTD)_{800}(NORCOOH)_{30}$  are shown in Figure 1. The figure clearly demonstrates that the cluster size can be increased by multiple passes through the process. It can also be seen from the micrographs that the clusters formed using the nanoreactor scheme are quite monodisperse and spatially confined.

Temperature of  $H_2S$  Reaction. Sankaran et al.<sup>26</sup> have described cluster formation within polymer films as a crystallization process. The cluster size should therefore depend on the kinetics of nucleation and growth. Increasing the temperature toward the melting point should decrease nucleation and increase the size of the clusters formed. The mobility of PbS within the polymer film should also be greater at higher temperatures, which should increase the size of the clusters formed. Figure 2 shows the HRTEM micrograph for PbS nanoclusters synthesized at high temperature in films of (MTD)<sub>800</sub>(NORCOOH)<sub>30</sub>, in which the lattice fringes can be clearly seen. In the figure, we see bunches of clusters (~4 nm in diameter) within domains (~12 nm in diameter).



**Figure 2.** HRTEM micrograph of the  $(MTD)_{800}(NORCOOH)_{30}$  diblock copolymer after reaction with  $H_2S$  at 140 °C.

Presence of Coordinating Solvents. The lead sulfide clusters in the acid-containing domains are stabilized by polymer-cluster interactions (probably by interactions with the carboxylic acid groups). If the  $H_2S$ reaction is carried out in the presence of a coordinating solvent such as pyridine, the solvent molecules can bind to the cluster in competition with the polymer.<sup>26</sup> A large excess of the solvent molecules could disrupt the polymer-cluster interaction almost entirely, by mass action. If the solvent does a poorer job of stabilizing the cluster than the polymer, nucleation theory anticipates an increase in the resulting cluster size.<sup>26</sup> TEM micrographs for PbS cluster formation in (MTD)<sub>500</sub>-(NORCOOH)<sub>20</sub> films (wormlike morphology), in the presence and absence of pyridine, are shown in Figure 3. The figure clearly shows the increase in cluster size when the reaction is carried out in the presence of pyridine.

 $H_2S$  Exposure Time. As previously mentioned, on exposure to  $H_2S$ , the lead-loaded films turn yellow within a minute and then turn orange. The change in color from yellow to orange is caused by the red-shift of the absorption edge with increasing cluster size. When the yellow polymer films are removed from the  $H_2S$ containing bomb reactor, no further color change takes place in the films, indicating that the color change from yellow to orange is not simply due to aggregation of existing small clusters. The time of exposure to  $H_2S$ can therefore be used to control the size of the clusters formed within the nanoreactor. This is analogous to varying the reaction time and therefore the extent of reaction in a conventional chemical reactor.

**UV–Vis Spectroscopy.** The previous section described how the color of the polymer films could be used to monitor cluster size. As cluster size increases, UV–vis spectroscopy can be used to detect red shifts in the absorption edge, thereby confirming the conclusions regarding the effects of the various processing parameters on cluster size.

Figure 4 shows UV–vis spectra for solid films of  $(MTD)_{500}(NORCOOH)_{20}$  (spherical morphology) containing PbS nanoclusters synthesized in the manner described above. The smallest clusters are those formed

Synthesis of PbS Nanoclusters



**Figure 3.** Representative micrographs of the  $(MTD)_{500}$ -(NORCOOH)<sub>20</sub> diblock copolymer with the wormlike morphology after PbS nanocluster formation: (a) in the presence of pyridine; (b) in the absence of pyridine.

at room temperature, after a single pass through the process. Their absorption edge is at the shortest wavelength. A second pass through the process causes an increase in cluster size, and as a result the absorption edge is red-shifted. Synthesis in the presence of pyridine results in an even greater increase in cluster size and hence a greater red-shift in the absorption edge. Our previously mentioned theoretical model<sup>14</sup> can be used to estimate the cluster size from the absorption threshold. The cluster sizes of 1.7 and 2 nm predicted by the model for the cases of single and double loading are in the same range as the sizes deduced from TEM.

We have discussed the effects of various processing parameters on cluster formation within identical nanoreactors. It is also interesting to determine the effect of the nanoreactor size on cluster size. Polymers B and C (500/20 and 800/30) both have spherical morphologies, but the size of the diacid domains is larger for polymer C ( $\sim$ 12 vs  $\sim$ 9 nm). Hence the size of the clusters formed in polymer C should be greater. Figure 5 shows UV–



Wavelength (nm)

**Figure 4.** UV–vis spectra for PbS-nanocluster-containing films of the  $(MTD)_{500}(NORCOOH)_{20}$  diblock copolymer with spherical morphology: (a) 1 loading; (b) 2 loadings; (c) 1 loading in the presence of pyridine.



Wavelength (nm)

**Figure 5.** UV–vis spectra for PbS nanoclusters synthesized by 2 loadings within films of (a)  $(MTD)_{500}(NORCOOH)_{20}$ diblock copolymer with spherical morphology and (b)  $(MTD)_{800}$ -(NORCOOH)<sub>30</sub> diblock copolymer with spherical morphology.

vis spectra for PbS nanoclusters synthesized within films of polymers B and C. As expected, the absorption edge for clusters synthesized within polymer C is more to the red, showing that the cluster size increases as the nanoreactor size increases, other conditions being held constant.

**WAXD.** Wide-angle X-ray diffraction is another tool that can be used to characterize the nanoclusters. Figure 6 compares the diffraction patterns for PbS nanoclusters synthesized within (MTD)<sub>800</sub>(NORCOOH)<sub>30</sub> with those for bulk PbS. The broad peak from 10 to 20° is due to amorphous scattering from the polymer.<sup>26</sup> The other peaks in the diffraction pattern for the films are at the same positions as those in the pattern for bulk PbS, thereby confirming the formation of crystal-line PbS nanoclusters. The finite size of the nanoclusters causes broadening of the WAXD peaks. The width of the peaks is inversely related to cluster size by



**Figure 6.** WAXD pattern for (a) films of  $(MTD)_{800}$ -(NORCOOH)<sub>30</sub> containing PbS nanoclusters synthesized in the presence of pyridine, (b) films of  $(MTD)_{800}$ (NORCOOH)<sub>30</sub> containing PbS nanoclusters synthesized by H<sub>2</sub>S reaction at 140 °C, and (c) bulk PbS powder.

Scherrer's formula.<sup>35</sup> The peaks for the film treated with  $H_2S$  at high temperature are narrower, implying that the size of the clusters formed by high-temperature  $H_2S$  treatment is greater than the size of the clusters formed by  $H_2S$  treatment in the presence of pyridine. Application of the Scherrer formula gives cluster sizes of 3 nm for the nanoclusters synthesized in the presence

of pyridine, and 4.3 nm for the nanoclusters synthesized at high temperature, in reasonable agreement with TEM results.

### Conclusions

We have demonstrated the synthesis of relatively monodisperse PbS clusters within diblock copolymer nanoreactors. The size of the clusters can be varied by varying parameters such as temperature, the presence of coordinating solvents, nanoreactor size, and the H<sub>2</sub>S exposure time. The universal scheme of synthesis also enables us to increase the cluster size by multiple passes through the process. These methods of varying cluster size could be used to tune the wavelength of emission of the cluster-containing films. The efficiency of emission is often reduced by traps and defects present at the surface of the cluster; therefore, the surface must be passivated to increase the efficiency. The universal scheme may enable surface passivation by coating the surface of the PbS nanocluster with another semiconductor produced by a second pass through the process. We are currently investigating the optical properties of the PbS nanoclusters.

**Acknowledgment.** We thank M. Frongillo of the C.M.S.E.-Electron Microscopy Facility at M.I.T. for assistance in HRTEM studies. R.S.K. also thanks the NSF for his graduate fellowship. This research was supported by NSF primarily under Grant CHE-9312413, and in part by Grant DMR-9022933.

CM960072I

<sup>(35)</sup> Kakudo, M.; Kasai, N. X-ray Diffraction by Polymers, Kodansha Ltd.: Tokyo, 1972.