Synthesis of CdS Nanoparticles in Solution and in a Polyphosphazene Matrix

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The synthesis and characterization of a polymer composite system containing quantum-confined II−VI semiconductor particles entrapped in a polyphosphazene network is discussed. A hybrid material was constructed using a guest:host approach in which the ion transporting ability of $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEP) and MEEP-like polymers was exploited to allow the formation of matrix-encapsulated, nanometer-sized CdS particles. As a first step, a cadmium thioglycolate precursor $[Cd_{10}(SCH_2CH_2OH)_{16}](NO_3)_4$ was found to react in solution to generate stable, soluble, CdS particles. These particles were characterized and found to be 25 Å in diameter. They exhibited an absorption at 362 nm, which was blue-shifted relative to the absorption of bulk CdS. This indicates a quantum confinement effect associated with nanometer-size particles. Second, a method was developed for the incorporation of CdS particles into a cross-linked polyphosphazene-based polymer network, and CdS particles were successfully grown within these polymer films. The CdS-containing polyphosphazene films were transparent and homogeneous. However, no significant control was achieved over the particle size dispersity. The polymer-encapsulated particles were larger than the solution-synthesized ones, with an average diameter of 70 Å diameter. They demonstrated a correspondingly smaller blue shift in the absorption spectrum, with an absorption at 470 nm. The morphology of these particles was examined.

Introduction

Quantum Effects in Nanostructures. Within the past 20 years, a new field of research has developed around the synthesis and characterization of materials that have nanometer-size domains or phases in 1-, 2-, or 3-dimensions.[1] These materials are important because, in some instances, many of their physical and chemical properties show a particle size dependence.[1a] In particular, considerable interest has centered on the synthesis of nanometer-size semiconductor particles.[2] The unique electronic and optical properties of semiconductor materials constitute the fundamental reason behind their technological importance.[3] For nanometer-proportioned systems, these optical and electronic properties become size-dependent.[4] Thus, chemical control over the growth and size of a particle should allow a corresponding control over these properties.

Synthesis of Nanostructures. These materials can be prepared in a variety of ways, and many syntheses of semiconductor nanoparticles are known, especially for (II−VI) systems such as ZnS and CdS.[5,6] Control over both the size and the polydispersity of the particles is important. Two approaches exist for the growth of semiconductor materials of nanometer sizes. The first involves the isolation and stabilization of small clusters through surface passivation in solution, or in a solid-phase matrix.[5f−7] In work by Bawendi, nearly monodisperse II−VI semiconductor particles are obtained using these techniques.[6a] These monodisperse particles have been shown to have the capacity to organize into superlattice structures with faceted features and well-defined sizes.[6b] The second approach involves the

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synthesis of a molecular-organometallic species with a fixed A:B elemental stoichiometry, analogous to the composition of the bulk semiconductor compound. Thermal decomposition then yields the desired inorganic material.[1b,c,9] This method has been more broadly applied to the formation of thin films.[1b,c] Work has particularly focused on the synthesis of III−V systems in order to find suitable single-source precursors to replace the hazardous reagents that are currently used to produce these species.[8]

It has been established that a combined use of a single-source precursor and the matrix entrapment method is possible.[7m,w,x,10,11] In such combined approaches, the potential exists for control over both the size and dispersity of the particles produced within a given sample. Polymers may be the best choice for host materials because they can be designed to yield a variety of bulk physical properties.[7m,q]

Polymer Matrixes. Many polymers have been investigated as media to control the growth of a variety of inorganic species including metal clusters.[7e,l,q,u,v,12a−e] The encapsulation of semiconductor particles within a bulk structure has several advantages over solution-based particle synthesis. Solid matrixes retain their shapes and do not spill or leak. Polymeric materials can be processed or manipulated into bulk structures. Polymers can be stretched and oriented, which may result in the physical alignment of the polymer chains into crystalline domains[13] and this could allow the construction of ordered arrays of the incorporated particles. Such structures would have a number of potential applications.[4a,b,14a,b]

The use of a polyphosphazene as a suitable host polymer to control the growth of nanometer-size semiconductor particulates is proposed for a variety of reasons. Polyphosphazenes contain a phosphorus−nitrogen backbone with two organic side groups linked to every phosphorus atom. The physical properties of the polymers depend significantly on the choice of the side groups (R).[15] The −P=N− backbone is thermooxidatively stable, and optically transparent in the region between 220 and 800 nm.[16] In addition, the well characterized poly[bis[2-(2′-methoxyethoxy)ethoxy]phosphazene] (MEEP) is currently being used as a solid-state polymer electrolyte in applications which require a high level of ionic conductivity.[17] This is considered to be a key property for polymer-controlled particle growth.[12a−c] The nature of the side-group structure in MEEP makes this polymer soluble in water and in a variety of organic solvents.[17a,18] The high flexibility of MEEP and similar polyphosphazenes is well-known (MEEP, $T_g = -85$ °C), and such systems maintain high ionic conductivity even after subsequent cross-linking is carried out.[19]

Results and Discussion

I. Growth of Quantum-Confined CdS Particles. Synthesis of a CdS Precursor. A search was conducted for a Cd:S molecular precursor that could be used to form CdS nanoparticles, based on the large number of methods known for the solution synthesis of CdS particles. The growth of nanometer-size CdS particles using thioalcohols as stabilizing agents[5i,k] was especially pertinent based on reports of cadmium thioglycolate complexes, which are multinuclear species with a fixed Cd:S ratio.[20] Pendent OH functionalities are present in such complexes and these could be used to carry out chemical derivatization procedures.

$$\mathrm{Cd(NO_3)_2} \xrightarrow[\mathrm{THF}]{\mathrm{2HSCH_2CH_2OH}} \underset{\mathbf{1}}{\mathrm{[Cd_{10}(SCH_2CH_2OH)_{16}](NO_3)_4}} \qquad (1)$$

To synthesize this molecular precursor, cadmium nitrate was treated with excess mercaptoethanol (eq 1). The nitrate salt was chosen because of its greater solubility than the cadmium halides, which are known to ionize only partially in solution.[21] A white precipitate was isolated which was soluble in water, methanol, and dimethyl sulfoxide (DMSO). Attempts to detect a

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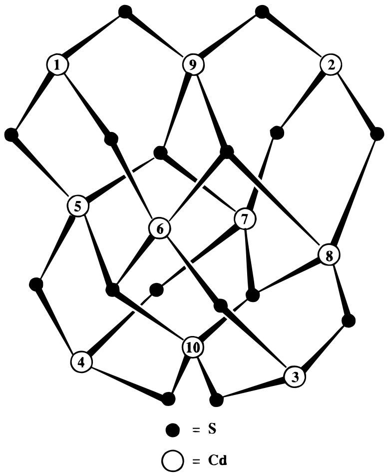

Figure 1. Structure of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$.

melting point for this material were unsuccessful because it decomposed to a yellow solid above 300 °C. Elemental analysis suggested an empirical formula $Cd_5S_8C_{16}H_{40}N_2O_{14}$. Attempts to obtain a suitable crystal for a single-crystal structure determination were unsuccessful. However, other methods of characterization were used to confirm that this material was the multinuclear complex (**1**), $[Cd_{10}(SCH_2CH_2OH)_{16}](NO_3)_4$, which has been previously reported.[20,22] This compound has a metal-based core with an extensively bridged network structure of ligands, which are bidentate in the solid state.[22c] For clarity, only the cadmium and sulfur atom core is shown in Figure 1. This compound is known to have four cadmium atoms (1−4) hexacoordinate, with octahedral geometry (O_h), four cadmium atoms (5−8) pentacoordinate, in a trigonal bipyramidal geometry (T_{bp}), and two cadmium atoms (9−10) tetracoordinate, in a tetrahedral geometry (T_d).[2,22c]

NMR Spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra of **1** were found to correspond to that of the starting reagent, 2-mercaptoethanol. This is in agreement with (SCH_2CH_2OH) chelation to Cd. No resonances were detected in the ^{1}H NMR spectrum of **1** that would correspond to the SH functionality. The analysis of compound **1** by ^{113}Cd NMR was conducted, and this revealed two resonance signals in the solution spectrum of **1**. The signals were singlets at 565 and 432 ppm and were present in a 3:2 ratio. The chemical shifts were in close agreement with results reported previously for the related compound $[Cd(SCH_2CH_2OH)_{16}](ClO_4)_4$ but were shifted downfield by approximately 50 ppm.[22a] This is acceptable based on previous work which revealed that the chemical shifts for the Cd resonance signals in the multinuclear Cd−thioglygolate complexes are influenced by both the concentration and the type of counterion present in solution.[22a] Assignments of the spectral peaks of **1** were made based on a comparison to values for the analogous perchlorate structure. The signal at 432 ppm was attributed to the Cd atoms with O_h coordination. The signal at 565 ppm was attributed to contributions from both the four T_{bp} and the two T_d coordinate Cd atoms. At ambient temperature in solution, the T_{bp} and T_d Cd atoms can undergo site interchanges and therefore give a single peak in the spectrum.

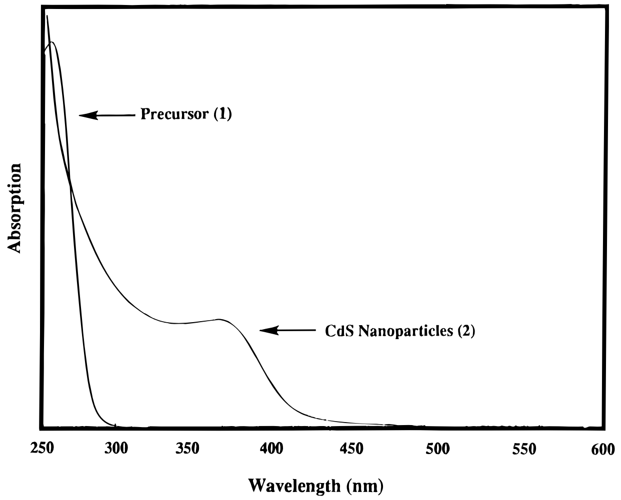

Figure 2. UV−visible spectrum comparison of the molecular precursor (1) with that of solution synthesized CdS particles (2).

Infrared Spectroscopy. Examination of the infrared spectrum of **1** confirmed the structure proposed for the multinuclear complex. A prominent stretching mode around 3500 cm^{-1} indicated the presence of OH functionalities. Aliphatic (CH) stretches were present near 3100 cm^{-1}, arising from the CH_2 units of the SCH_2CH_2OH ligand. The NO_3 stretch at 1384 cm^{-1} was also seen. However, the SH stretch, which was prominent for 2-mercaptoethanol (2571 cm^{-1}), was absent from the infra red spectrum of **1**.

UV−Vis Spectroscopy. The optical absorption spectrum of **1** gave a maximum absorption at 254 nm (Figure 2). This is in agreement with previous reports for similar $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ structures.[22a]

CdS Cluster Formation. The precursor compound, **1**, was treated with an excess of Na_2S (3.3:1 mole ratio of S to Cd) in aqueous solution to generate stable, soluble, cadmium sulfide particles of nanometer dimensions (eq 2). Formation of a white, turbid solution occurred during the initial addition of Na_2S to **1**. However, further addition of Na_2S induced a clearing of this solution and a color change from light blue to a bright yellow. The particles formed in this way were soluble and remained stable in aqueous solution for several months. These particles can be prepared in high concentrations (10^{-3} M) and diluted to lower concentrations (10^{-5} M) with water, alcohols, or a variety of water-miscible organic solvents, without the loss of solubility. Following acidification, aggregation occurred and the particles precipitated from solution.

$$[Cd_{10}L_{16}](NO_3)_4 \xrightarrow{\text{excess } Na_2S} \underset{\mathbf{2}}{\text{CdS particles}} \qquad (2)$$

$$L = SCH_2CH_2OH$$

Particle Sizes and Size Distributions. TEM spectroscopy (Figure 3) was carried out on a sample of particles obtained from solution (10^{-5} M in 95% ethanol). Inspection of the micrographs indicated that polydisperse CdS particles had formed with diameters less than 100 Å. Some very large particles (50−100 Å) were seen, but about 75% of the sample was found to

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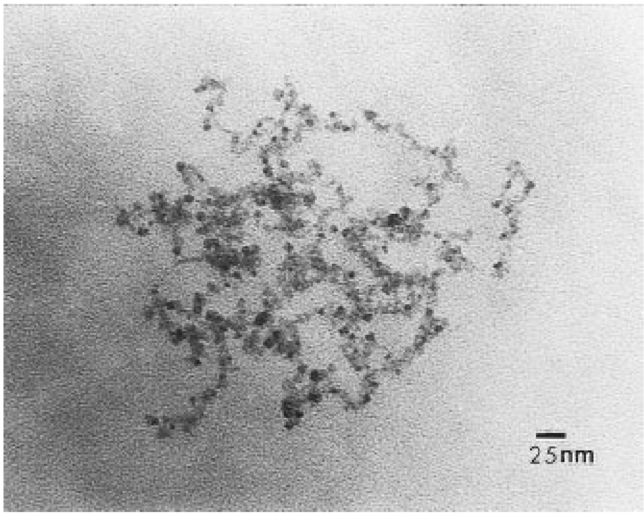

Figure 3. Transmission electron microscopy of solution-synthesized CdS particles (2).

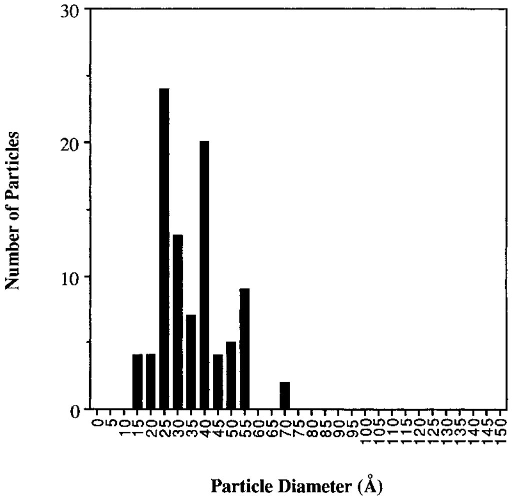

Figure 4. Particle size distribution map of solution-synthesized CdS particles (2).

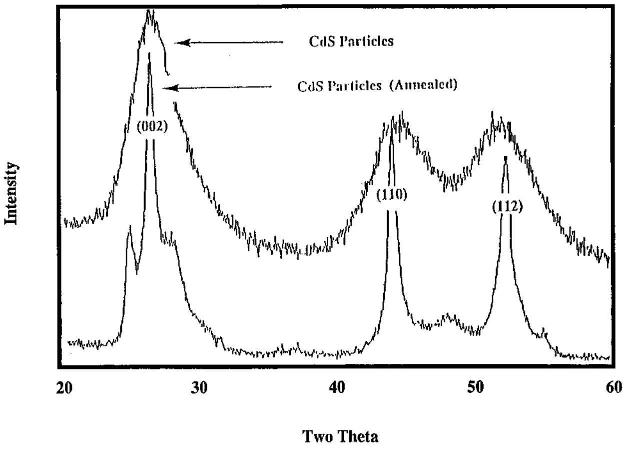

Figure 5. X-ray diffraction pattern of solution-synthesized CdS particles (2).

contain particles between 25 and 50 Å diameter in size. A map of the particle sizes is shown in Figure 4.

Particle Morphology. The CdS clusters could be isolated as a yellow solid that allowed X-ray powder diffraction to be conducted (Figure 5). Diffraction peaks were obtained which were broadened relative to those from a sample of bulk, crystalline CdS. This broadening has been attributed to the small size of the nanoparticle rather than a decreased crystallinity, and this is in agreement with the small size of the particles detected in the TEM.[5h,6]

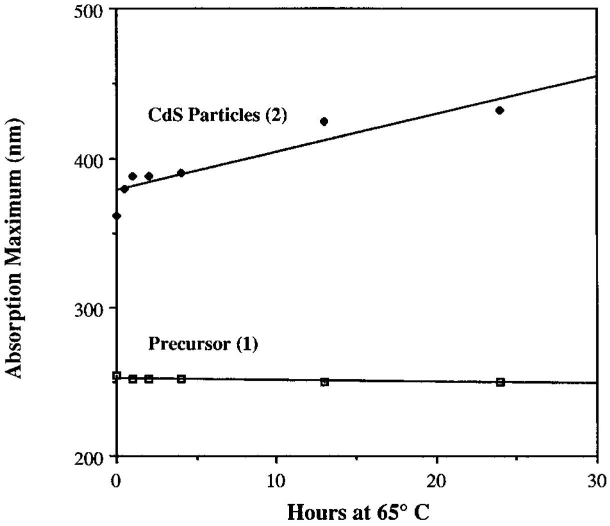

Figure 6. Comparison of the solution stability of molecular precursor 1 with CdS particles (2) at 65 °C.

Thermal annealing of the sample caused the diffraction peaks to sharpen. Peaks could be identified which corresponded with reflections from the (001), (110), and (112) lattice planes of cubic-phase CdS. However, the formation of a small percentage of hexagonal-phase CdS was also indicated. It was unclear from this experiment alone whether the partial hexagonal phase exists within the nanoparticles before thermal annealing, or if it arises as a result of a rearrangement of the particle lattice during thermal annealing. Most syntheses of nanoparticles of CdS have yielded only cubic-phased particles.[2c] Therefore, a synthetic method that offers the potential to generate hexagonal phase CdS nanoparticles is of interest.

UV−Vis Spectroscopy. Examination of the UV−vis spectrum (Figure 2) of a solution of nanoparticles indicated a blue shift in the optical absorption maximum (362 nm), relative to the absorption of bulk CdS (512 nm). Calculations of the average particle size were made employing the Brus formula.[23] Estimations based on this absorption maximum suggested the presence of particles with an average diameter of 30 Å. This is in close agreement with the sizes observed in the TEM analysis.

The stability of these CdS clusters in solution was also examined. Aqueous solutions of both **1** and CdS particles were heated at 65 °C for 24 h. The changes in the optical absorption spectra were monitored and the results are shown in Figure 6. Heating brought about a red shift in the absorption maximum. This indicated that cluster growth to larger sizes had occurred, possibly through aggregation. Estimations of the average particle size after heating were again made using the Brus formula and these indicated particles of 50 Å diameter.[23] In comparison, it appeared that **1** was thermally stable in solution and did not undergo any type of self-initiated reaction or decomposition to form CdS clusters or bulk CdS.

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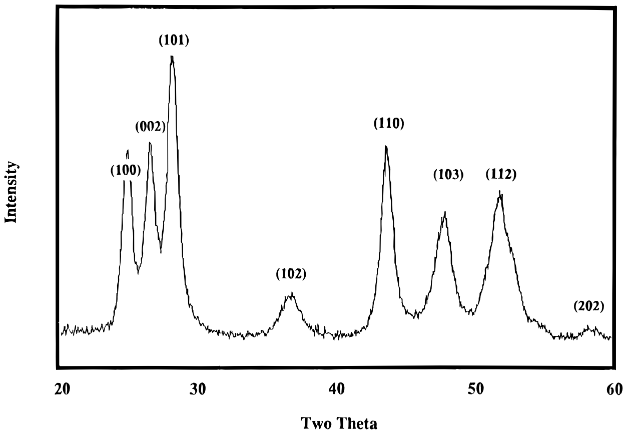

Figure 7. X-ray diffraction pattern of annealed molecular precursor (1).

Comments on Particle Growth. Several aspects of the reaction of **1** with excess Na_2S are interesting and may yield an insight into the formation of CdS nanoparticles. The following facts have been established: (1) Exposure of **1** to Na_2S in solution yields CdS particles with a mixed phase morphology containing some hexagonal but predominantly cubic-phase CdS. However, powder X-ray diffraction studies conducted on **1** indicated that it is a crystalline, molecular material which forms hexagonal-phase CdS following thermal annealing (Figure 7). (2) An excess of Na_2S is necessary for the formation of CdS particles. A stoichiometric reaction of Na_2S with **1** does not give CdS particles. (3) The formation of stable, soluble CdS particles requires a basic pH. CdS particles do not form from the reaction of **1** with a solution of excess NaHS (adjusted to pH = 7). Moreover, the acidification of an aqueous solution of CdS particles results in the aggregation and precipitation of these particles from solution.

A hexagonal type of morphology would be expected to arise in the CdS nanoparticles if their growth occurred through a straightforward aggregation of **1**. Therefore, particle formation must not occur through a building-block assembly of units of **1** alone. It is suspected that **1** undergoes a partial breakdown before CdS particles are formed. A possible mechanism is similar to the one suggested by Schwarzenbach, which involves the base complexation of polynuclear cadmium thioglycolates, and is related to one proposed by Swayambunathan, for the reaction of Cd^{2+} with H_2S.[5j,20] In aqueous solution, excess Na_2S generates HS^- and OH^-. The OH^- ions coordinate to $[Cd_{10}L_{16}]^{4+}$ at the four Cd(O_h) sites, to form the neutral compound $[Cd_{10}L_{16}(OH)_4]$. The high concentration of Na_2S allows this species to be coordinated further (either by an additional four HS^- units or by OH^- ions), at the four Cd(T_{bp}) sites, to give a highly charged and unstable unit which has a tendency to dissociate. This dissociation probably occurs with the formation of $CdL_4{}^{2-}$ and the neutral species $[CdS]CdL_2$. The neutral species could aggregate to form $[CdS]_x(CdL_2)_x$. The negatively charged moiety, $CdL_4{}^{2-}$, may act to stabilize the particles formed in solution.[5j]

Such a mechanism for CdS particle growth could explain the solution stability of **1** and would account for the need for basic pH, excess Na_2S, and the lack of reaction of **1** with NaSH, to give CdS particles. This mechanism can also account for the aggregation and precipitation from solution of CdS particles following acidification, since acidification of a solution of particles would disrupt the ability of mercaptoethanol to complex and stabilize the particles in solution. This mechanism may also explain the presence of a partial hexagonal phase morphology in the CdS particles. According to this mechanism of particle growth, a primary building block in the assembly of CdS particles is the moiety $[CdS]CdL_2$. Such units are believed to aggregate, forming $[CdS]_x(CdL_2)_x$. It seems likely that the CdL_2 segments are not simply neutral species, loosely complexed to the CdS particle, but are in fact covalently bound to the particle surface.[5g,j,l] Such bonding would give rise to a $(\mu_4\text{-S})_2Cd(\mu_1\text{-SR})_2$ coordination for the surface-bound layer of cadmium atoms of any particle. This coordination is surprisingly similar to the $(\mu_3\text{-SR})_2M(\mu_1\text{-SR})_2$ geometrical arrangement that has been suggested by Dance as a necessary building unit for the generation of hexagonal morphologies.[24] In reality, a complex behavior involving several types of mechanisms for particle growth may contribute to the formation of CdS particles. This would be the most likely explanation for the mixed morphology seen for the nanoparticles.

II. Particle Encapsulation in Polymer Films.

Polymer Matrix Procedure. An attempt was made to synthesize CdS nanoparticles within a polymer matrix, in an effort to gain control over the particle size dispersity. A two-step approach was taken which is outlined in Scheme 1. The first step involved the assembly of a cross-linked polymer-precursor structure. Then, in the second step, CdS nanoparticle growth was induced within this structure. To employ the particle growth method described in the first part of this paper, it was necessary to use a hydrophilic polymer that would be chemically compatible with the precursor species **1**. Derivatives of poly[bis[2-(2′-methoxyethoxy)ethoxy]-phosphazene] (MEEP) were chosen as the target polymers.[17,18] Such systems are water-soluble and have a high ionic conductivity in the solid state, and the ethyleneoxy component of the side-groups is chemically compatible with **1**. Thus, a cosubstituent polyphosphazene with a structure resembling MEEP was synthesized. This polymer was doped with **1** and was then treated in a manner that simultaneously cross-linked and covalently linked **1** to the polymer to form a network species. Subsequent exposure of this structure to an aqueous solution of Na_2S resulted in the growth of CdS particles within the polymer network.

Polymer Synthesis. The cosubstituent polymer synthesized is shown as **6**. Polyphosphazene **6** was randomly substituted by the two reagents and contained aliphatic OH functionalities on 50% of the side groups. This functionality provided both compatibility and a reactive site to form cross-links with **1** or with other side-group OH functionalities. The mixed substituent polymer system was more convenient to work with in terms of its stability and solubility. Attempts were also made with a single substituent polyphosphazene which contained OH functionalities on every side group. However, this system had only a limited solubility and underwent molecular weight decreases over time.[25] Polymer **6** was soluble in polar, protic solvents such as

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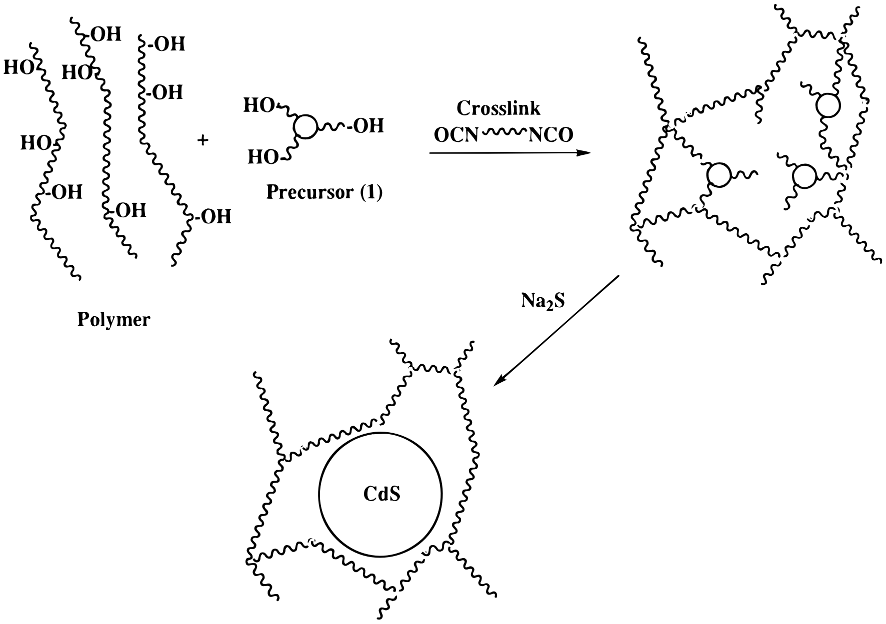
(24) Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6285−6295.

(25) Delprato, C.; DeJaeger, R.; Houalla, D.; Potin, Ph. *Macromolecules* **1995**, *28*, 2500−2505.

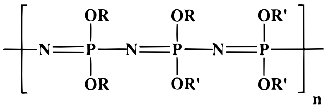
Scheme 1



H_2O and alcohols. It was also soluble in dioxane, and in several other high-boiling, polar, aprotic solvents, but it was insoluble in THF.

OCN-$CH_2CH_2OCH_2CH_2OCH_2CH_2$-NCO

4



$$\left[-N=\underset{OR}{\overset{OR}{P}}-N=\underset{OR'}{\overset{OR}{P}}-N=\underset{OR'}{\overset{OR'}{P}}- \right]_n$$

6

R = -$CH_2CH_2OCH_2CH_2OCH_3$

R' = -$CH_2CH_2OCH_2CH_2OH$

Cross-Linking Reagent. A diisocyanate was chosen as the cross-linking agent for use in the first step of this procedure. Diisocyanates can react with alcohols to form stable urethane linkages.[26] However, diisocyanates react with other active proton sources as well. Thus, all cross-linking reactions were carried out under anhydrous conditions.[26] Diisocyanate **4** was synthesized. The ethyleneoxy component of **4** was designed to be compatible with the side-group structure of polymer **6**. This compatibility was essential in order to form transparent, cross-linked films. Attempts to make transparent films using the commercially available hexamethylenediisocyanate were unsuccessful. Aromatic diisocyanates could not be used because they reacted to form a network structure before films could be cast.[27]

Film Formation. The effects of polymer entrapment on CdS particle growth were examined in two systems. The first of these systems (A) had polymer **6** and **1** directly cross-linked together into a network structure via the diisocyanate. The second system (B) had polymer **6** as a diisocyanate cross-linked network, which was then saturated with but not directly linked to **1**. Cadmium sulfide nanoparticles were formed following the exposure of films from both of these systems to Na_2S. These films were then characterized using TEM and UV−vis spectroscopy.

Films were cast from solution using a ratio of **6** to **4** in proportions that should yield networks with a 50% cross-linked density. Evaporation of the solvent then gave polymer films that were structurally stable. These films were very flexible and underwent swelling in water but did not dissolve. They were stable in basic pH (7−9) for at least a month without loss of structural integrity or transparency.

Particle Growth. The exposure of samples from system A to excess Na_2S resulted in the formation of transparent and colorless films. This suggested that very little CdS formation had occurred. Exposure of samples from system B to excess Na_2S yielded films that were transparent but bright yellow in color. This implied that a significant amount of CdS particle formation had occurred. TEM analyses were performed on thin sectioned samples from both systems A and B. In both cases, particle formation was found to occur homogeneously throughout the samples. However, the density of particle formation was much greater in films obtained from system B than it was from system A. This was in agreement with the different color changes observed in the two film systems.

The limited particle growth in system A films can be explained by inhibition of diffusion. For example, a straightforward reaction of **1** with Na_2S would occur by a breakdown of **1** into two products, the neutral species $[CdS]CdL_2$ and CdL_4^{2-} anions. In solution, the CdL_4^{2-} anions can separate from each other through diffusion-driven processes. However, diffusion-driven processes may be hindered in system A films due to the cross-linking of **1** into the polymer network. Thus, **1** may no longer undergo the normal breakdown, since this would result in the formation of a polyanionic polymer−CdL_4^{2-} chain. These bound anions would be incapable of undergoing diffusion to lower their Coulombic repulsions. As a consequence, no pathway is favored for the

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(26) *The Chemistry of Cyanates and Their Thio Derivatives*; Patai, S., Ed.; John Wiley and Sons: New York, 1977; Part 2, Chapter 17.

(27) Attempts were made to use toluene 2,4-diisocyanate as a cross-linking agent. However, upon addition of this reagent to a solution of polymer **6** in dioxane, immediate gelation of the solution occurred. Consequently, no other attempts were made to use aromatic diisocyanates as the cross-linking agent.

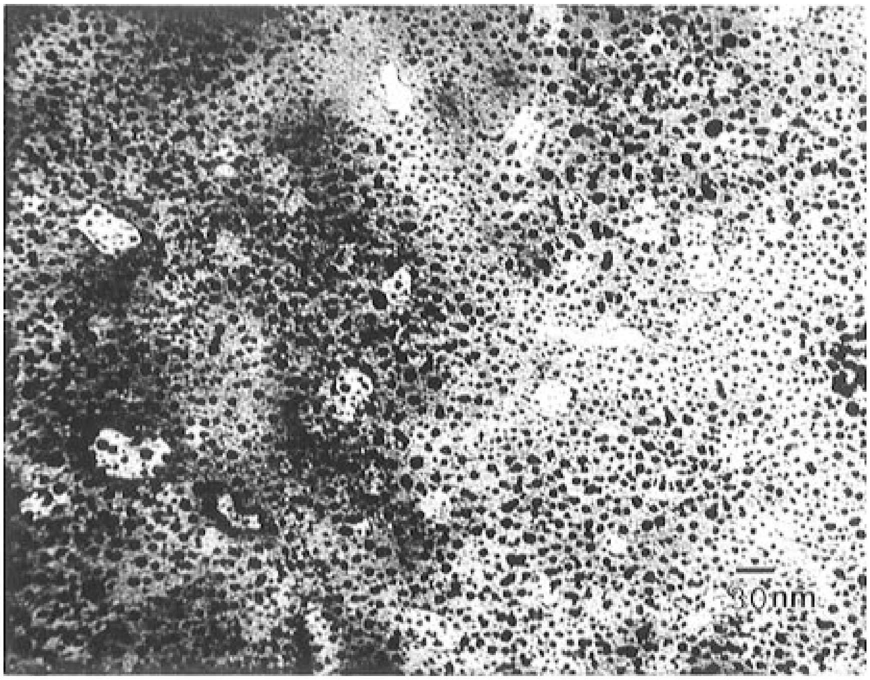

Figure 8. Transmission electron microscopy of polymer-encapsulated CdS particles.

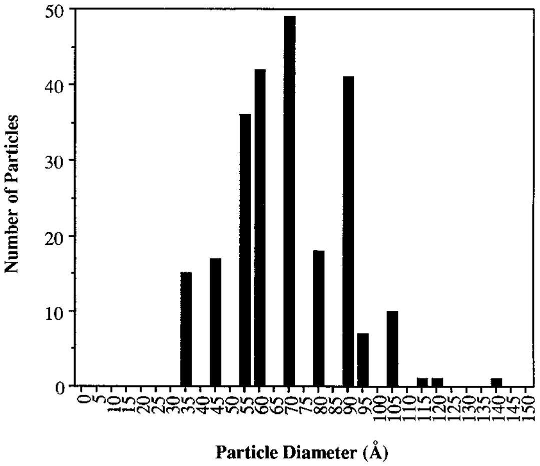

Figure 9. Particle size distribution map of polymer-encapsulated CdS particles.

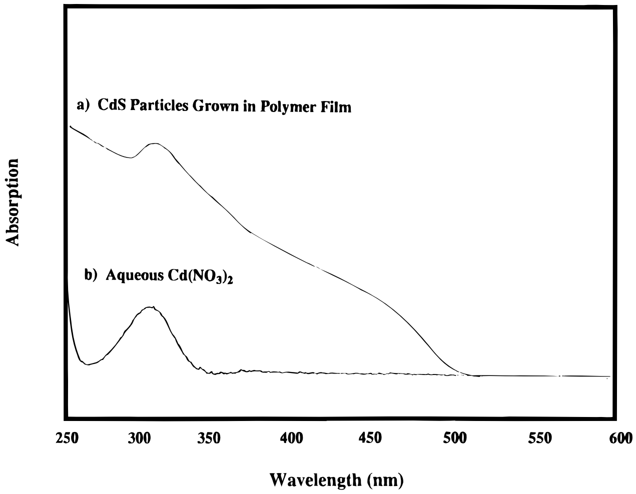

Figure 10. UV−visible spectroscopy of polymer-encapsulated CdS particles.

reaction of **1** with Na_2S to form CdS particles.[28] Therefore, the density of particle formation in system A films is greatly reduced. This scenario would not apply to the system B films. Here, there are no cross-link-hindered diffusion processes associated with the reaction of **1** with Na_2S, and **1** can undergo conversion to CdS particles. Thus, it would be expected that the density of particle formation is greater in the system B films. For convenience, further particle characterization was conducted on the system B films only. The presence of both Cd and S in these films was confirmed through X-ray microanalysis in the areas where particle formation was detected. TEM photographs of thin sectioned samples from system B films are shown in Figure 8.

Particle Sizes and Dispersity. Samples of system B films were examined, and CdS particles with polydisperse sizes were detected in these films. The particle size distribution is mapped in Figure 9. The average particle sizes formed inside the polymer films were between 70 and 90 Å in diameter. Particles with these dimensions are below the size where the bulk properties of CdS are fully developed.[29] However, these particles were larger than those produced by the solution-based method discussed earlier. The larger sizes could indicate that particle aggregation is somehow enhanced in the polymer films compared to reactions in solution. The morphology of the film-based CdS particles was also investigated by electron diffraction experiments. These indicated the presence of mixed hexagonal and cubic phase CdS throughout the sample.

UV−Vis Spectroscopy. The UV−vis spectrum for the system B films is shown in Figure 10. These films had an absorption onset at 470 nm, which was attributed to the presence of CdS particles in the films. This absorption indicated that larger sized particles were present within the film than in the solution-derived system (362 nm), but were still blue-shifted

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(28) Allcock, H. R.; Klingenberg, E. H.; Welker, M. F. *Macromolecules* **1993**, *26*, 5512−5519.

(29) Brus, L. *IEEE J. Quantum Electron.* **1986**, *QE-22(9)*, 1909−1914.

relative to the bulk material (512 nm). The absorption at this wavelength implied a particle size of 70 Å diameter. This is in good agreement with the average particle size distribution obtained through TEM analysis.

The absorption spectrum for an aqueous solution of $Cd(NO_3)_2$ is also shown in Figure 10. This salt showed a very strong absorption below 250 nm, but with another less intense absorption at 300 nm. To highlight this feature, the spectrum shown in Figure 10 has been expanded in the 250−600 nm region. This very weak absorption at 300 nm was attributed to $[Cd(OH)]^{1+}$, a species which arises from the hydrolysis reaction of cadmium oxo salts in aqueous solution (eq 3).[30]

$$Cd^{2+} + H_2O \rightleftharpoons Cd(OH)^{+} + H^{+} \qquad [K_h = 10^{-10}] \qquad (3)$$

This reaction is well-known. Ordinarily, $[Cd(OH)]^{1+}$ is present in only small concentrations and it is hardly noticeable in the absorption spectrum. However, the addition of OH^- ions to an aqueous cadmium salt solution results in an increase in the intensity of this absorption. A similar feature (at 300 nm) was seen in the absorption spectrum for the polymer films that contained CdS particles. This feature is also believed to be due to the presence of $[Cd(OH)]^{+}$. The presence of this cationic species would support the mechanism proposed for the formation of CdS particles, which involves the breakdown of **1** through coordination with OH^- anions.

Conclusions

A cadmium thioglycolate precursor was shown to be capable of generating stable, soluble, CdS particles of nanometer sizes between 25 and 50 Å in diameter following treatment with Na_2S in water. A possible mechanism for particle growth has been proposed which can explain the mixed phase morphology found in the resultant particles.

The same precursor was then used for the successful incorporation of CdS nanoparticles into a bulk polyphosphazene matrix. A cosubstituent polyphosphazene was synthesized, and a reaction method was designed and used to conduct the formation and growth of polymer-supported CdS nanoclusters with a size of approximately 70 Å in diameter. Optically transparent, cross-linked, polymer films, containing CdS particles evenly distributed throughout the material were synthesized. These films were homogeneous and showed no phase separation. However, fine control over the polydispersity of these nanoparticles using this matrix-regulated growth method has not yet been realized. Characterization of the particles grown within the polymer films yielded further support for the overall mechanism of particle growth. Such an understanding is beneficial for future efforts to control the sizes, morphologies, and dispersities of nanoparticles formed in solution or polymeric media. For example, variations in polymer cross-link density, solvent, or in the molecular precursor may improve the control over particle size and dispersity.

With this system there is the possibility that semiconductor nanoparticles can be grown in the presence of other optically or electronically interesting moieties because the polyphosphazene system allows multifunctional polymers to be synthesized quite easily.[15a] The methods employed in the formation of CdS within polyphosphazenes could be generalized to permit the synthesis of other nanocomposite hybrid systems, such as polymers that contain metal clusters or possibly III−V semiconductor particles.

Experimental Section

General. All chemicals and starting reagents were obtained from a commercial source (Aldrich), unless described differently. The organic solvents employed were used as received or were distilled from sodium spheres using benzophenone as an indicator of solvent dryness. Dichloromethane, 1,2-dichlorobenzene, and dimethyl sulfoxide (DMSO) were distilled from calcium hydride. The water used in the synthetic procedures was both distilled and deionized before use. Elemental analyses were by Quantitative Technologies Inc. (Whitehouse, NJ). The general procedure for the preparation of the starting $(NPCl_2)_n$ reagent is as described below.

Instrumentation. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker WM-360 spectrometer with the use of $CDCl_3$, THF-d_8, acetone-d_6, or D_2O (MSD Isotopes) either as the solvent or as an internal reference. UV−vis absorption spectra were recorded using a Shimadzu 310 PC, UV−NIS/NIR spectrophotometer. Infrared absorption spectra were recorded by means of a Perkin-Elmer 1710 infrared Fourier transform spectrometer, using either KBr pellets or a NaCl liquid cell. Gel permeation chromotography was carried out with an HP 1090 liquid chromatograph equipped with two Phenominex Phengel linear 10 columns and an HP 1047A refractive index detector. A 0.01 M solution of $(n\text{-Bu})_4N(NO_3)$ in THF was used as the elution solvent. Analysis of the chromatographs was conducted by means of an HP Chemstation equipped with Polymer Laboratories software. Molecular weights are reported versus polystyrene standards. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 unit controlled by a PE 7500 computer with heating rates between 10 and 40 °C/min and sample sizes of 10−30 mg. Transmission electron microscopy (TEM) and supporting work, including sample preparation, was carried out at the Electron Microscope Facilities in the Biotechnology Institute at The Pennsylvania State University. TEM was performed on a JEOL 1200 EXII at 80 KV operating voltage. X-ray microanalysis was carried out with PGT XMIX version 6. Samples were prepared for microtoming by impregnating films with firm-formulation epoxy resin from Spurr's Kit, which was obtained from Electron Microscopy Sciences. Thin sections with an average thickness of 800 Å were made using a LKBIII-8800 Ultramicrotome from LKB Instruments.

Preparation of Poly(dichlorophosphazene). Hexachlorocyclotriphosphazene (Ethyl Corp., Nippon Fine Chemical) was recrystallized from heptane, followed by vacuum sublimation (0.02 mmHg, 40 °C). This was then placed in a clean, dry, glass tube (200 g) which was sealed under vacuum. The sealed tube was heated in an oven fitted with a motorized rocking shelf (3 rocks/min) at 250 °C (18 h) to allow polymerization of the cyclic trimer. The tube was removed and cooled to room temperature. It was then cooled in liquid nitrogen and allowed to warm to room temperature three times before opening. This facilitated the removal of the polymer from the glass. The tube was then broken open under an argon atmosphere and the polymer was removed, cut into small pieces, and loaded into a sublimator. Residual $(NPCl_2)_3$ was removed by vacuum sublimation (0.02 mmHg, 40 °C). The remaining $(NPCl_2)_n$ was stored in an inert atmosphere. Yield 18.0% (38.39 g). ^{31}P NMR ($CDCl_3$ internal reference), δ (ppm) −17.20 (s).

Precursor and CdS Synthesis. *Synthesis of* $[[Cd_{10}(SCH_2CH_2OH)_{16}](NO_3)_4]$ *(1).* One equivalent of $Cd(NO_3)_2$ (6.12

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[30] Aylett, B. J. *The Chemistry of Zinc, Cadmium and Mercury*; Pergamon Texts in Inorganic Chemistry, Pergamon Press: Oxford, U.K., 1973; Volume 18, Chapter 3.

g, 0.02 mol) was dissolved in 100 mL of dry THF. To this stirred solution under argon was added dropwise at room temperature 2 equiv of mercaptoethanol (3.12 g, 0.04 mol) dissolved in 50 mL of dry THF. After the addition was complete, the mixture was stirred at reflux for 24 h by which time a white precipitate had formed. This reaction mixture was then cooled to room temperature and the solids were filtered off. The solids were washed several times with excess amounts of diethyl ether, and the resultant white powder was collected and dried under vacuum. Yield 46.87% (2.5 g, 0.001 mol), mp >300 °C decomp. ^{1}H NMR ($D_2O/CDCl_3$), δ (ppm) 3.76 (s, 2 H); 3.12 (s, 1 H); 2.93 (s, 2 H). ^{13}C NMR ($D_2O/CDCl_3$), δ (ppm): 62.3, 32.7. IR spectrum (KBr pellet), ν (cm^{-1}): 3387, 2926, 2873, 2426, 1767, 1634, 1455, 1384, 1284, 1216, 1157, 1052, 1006, 940. Elemental analysis % calcd for Cd: 43.39, S: 18.59, C: 13.90, H: 2.90, N: 2.70; found Cd: 44.83, S: 19.23, C: 14.91, H: 3.16, N: 2.15 (Cd:S ratio 1:1.6).

Synthesis of CdS Nanoparticles (2). An aqueous solution was prepared from 1.6 g (0.614 mmol **1**, 0.0061 mol Cd) in 2000 mL of water. To this was added dropwise at room temperature a solution of Na_2S (0.27 g, 0.0035 mol) in 500 mL of water, with high-speed stirring. When these two reagents were mixed together, a turbid, white solution formed initially. However, the turbidity decreased to the point that the mixture became clear and colorless at the end of the addition. An additional portion of Na_2S (0.54 g, 0.0069 mol) dissolved in 1000 mL of water was then added dropwise and the mixture became a bright yellow solution. This solution contained a molar ratio of Cd:Na_2S of 1:1.7, an overall ratio of Cd:S of 1:3.3, and was approximately 10^{-3} M concentration in CdS particles. The solution was placed in dialysis tubing (500 MWCO) and dialyzed against water for 96 h. This removed any excess and/or unreacted cadmium and sulfur reagent salts. The particles were collected, dried and characterized. Elemental analysis % calcd for Cd: 77.8, S: 22.2, C: <10.0, H: <0.1, N: <2.0; found Cd: 75.1, S: 20.2, C: 3.7, H: 0.8, N: 0.0 (Cd:S ratio 1:1).

Preparation of Polymer Side-Group and Cross-Linking Agent. *Synthesis of $HOCH_2CH_2OCH_2CH_2O-THP$ (**3**).* This side group was prepared from diethylene glycol in a manner reported in the literature for the protection of alcohols with dihydropyran.[31] One equivalent of diethylene glycol (42.4 g, 0.4 mol) was mixed with 1 equiv of dihydropyran (33.64 g, 0.4 mol) in 200 mL of dry dichloromethane. A small amount of *p*-pyridinium toluenesulfonate (PPTS) (1.0 g, 0.004 mol) was added to catalyze the reaction. This solution was stirred at 25 °C for 12 h. The product was isolated by removing the dichloromethane under vacuum. The tan-colored oily residue was dissolved in diethyl ether and extracted (3 times) with excess water. The diethyl ether layer was collected, dried over $MgSO_4$, and the ether removed by evaporation. The main side products from this reaction were the diprotected diol and unreacted starting reagents. The crude product was passed down a column of silica gel with a 50:50 hexane:diethyl ether solvent mixture as the eluent. The desired fraction containing the monoprotected diol was collected and the solvent removed. The purified product was then dried under high vacuum overnight, and a pale yellow liquid was obtained. Yield 21.9% (16.61 g, 0.087 mol.). ^{1}H NMR ($CDCl_3$), δ (ppm) 4.54 (q, 1 H); 3.77 (m, 2 H); 3.60 (m, 4 H); 3.52 (m, 3 H); 3.43 (m, 1 H); 2.99 (t, 1 H); 1.63 (m, 2 H); 1.46 (m, 4 H). ^{13}C NMR ($CDCl_3$), δ (ppm) 98.8, 72.3, 70.2, 62.1, 61.5, 30.3, 25.2, 19.3. IR spectrum (KBr cell/CCl_4), ν (cm^{-1}) 3475, 2944, 2873, 1458, 1354, 1261, 1202, 1185, 1128, 1078, 1037, 1021, 987. MS calcd for $C_9H_{18}O_4$ 190.0, found 190.0. Elemental analysis % calcd for C: 58.84, H: 9.47; found C: 58.96, H: 9.59.

*Synthesis of $OCNCH_2CH_2OCH_2CH_2OCH_2CH_2NCO$ (**4**).* In an argon-charged flask fitted with a reflux condenser and magnetic stirrer bar, a mixture of 2,2′-(ethylenedioxy)bis(ethylamine) (6.09 g, 0.04 mol) in 20 mL of dry 1,2-dichlorobenzene was added to a solution of phosgene (1.9 M, 150 mL) in toluene, at 0 °C. **[Danger: phosgene is a highly toxic gas.]** A colorless, viscous oil formed immediately. The mixture was stirred vigorously in order to prevent the oily product from adhering to the bottom of the flask. After the addition was complete, the solution was warmed gently to room temperature. Gaseous HCl was evolved from the reaction mixture. The solution was heated to 100 °C for 2 h, after which time the evolution of HCl ceased. To this mixture was added dropwise a solution of triphosgene (12 g, 0.04 mol) dissolved in 40 mL of 1,2-dichlorobenzene. After this addition was complete, the reaction mixture was heated to 115 °C. Phosgene and HCl gases evolved from the reaction mixture. The vessel was heated at the reflux temperature of the solvent for 12 h, after which time most of the solids in the reaction mixture had dissolved to yield a pale yellow-colored solution. The mixture was cooled to room temperature and the solids were filtered off from the mother liquor. The solvent was then removed under vacuum from the filtrate to leave a yellow oil. Attempts to distill this product under high vacuum were unsuccessful. The crude, oily product was dissolved in dry dichloromethane and was filtered with activated carbon to remove impurities. The solution mixture was then filtered through Fuller's earth, and the dichloromethane was removed under vacuum. The product was dried under high vacuum overnight and was obtained as a yellow liquid. Yield 44.0% (3.62 g, 0.018 mol). ^{1}H NMR ($CDCl_3$), δ (ppm) 3.65 (s, 4 H); 3.60 (t, 4 H); 3.36 (t, 4 H). ^{13}C NMR ($CDCl_3$), δ (ppm) 69.7, 69.6, 42.5. IR spectrum (KBr cell/CCl_4), ν (cm^{-1}) 3673, 3624, 3350, 3082, 2955, 2071, 2262, 1760, 1725, 1624, 1532, 1456, 1398, 1349, 1284, 1248, 1187, 1122, 1034, 987. MS calcd for $C_8H_{12}N_2O_4$ 200.0, found 200.0. Elemental analysis % calcd for C: 48.00, H: 6.00, N: 14.00; found C: 47.92, H: 6.21, N: 13.94.

Polymer Preparation. *Synthesis of $[(THP(OCH_2CH_2)_2O)(CH_3(OCH_2CH_2)_2O)PN]_n$ (**5**).* Poly(dichlorophosphazene) (4.0 g: 2.44 g Cl, 0.068 mol) reacted with reagents prepared from 1 equiv of **3** (7.50 g, 0.039 mol), 1 equiv of 2-(2-methoxyethoxy)ethanol (4.69 g, 0.039 mol) and 2 equiv of sodium metal (0.90 g, 0.039 mol). The sodium, freshly distilled 2-(2-methoxyethoxy)ethanol, and **3** were previously mixed together in 300 mL of dry THF, and were allowed to react at reflux (48 h) following standard procedures to form the corresponding sodium salts of the alcohols.[15b] The $(NPCl_2)_n$ was dissolved in THF (400 mL) and was added dropwise to this solution of sodium salts. When the addition of $(NPCl_2)_n$ was complete, the mixture was heated to reflux for 72 h. A white precipitate (NaCl) immediately formed and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. When no further change was evident, the mixture was cooled to room temperature. The polymer was concentrated by removal of two-thirds of the THF solvent. The thick, pale tan liquor was transferred into moistened, dialysis tubing (6−8000 MWCO). The polymer was first dialyzed for 24 h against water (the polymer was insoluble in this solvent and precipitated from solution), followed by dialysis against 95% ethanol for 96 h and then dialysis against 100% ethanol for an additional 48 h. After 1 week, the clear, colorless polymer solution was removed from the dialysis bag and filtered, and the solvent was removed under vacuum. The residual, rubbery solid was collected and dried under high vacuum. This polymer was a clear, pale yellow gel, very soluble in THF, chloroform, or alcohols. ^{31}P NMR ($CDCl_3$), δ (ppm) −7.74 (s). ^{1}H NMR ($CDCl_3$), δ (ppm) 4.56 (s, 1 H); 4.20 (s, 4 H); 3.78 (t, 2 H); 3.59 (s, 8 H); 3.52 (t, 4 H); 1.77 (m, 1 H); 1.68 (m, 1 H); 1.49 (m, 4 H). ^{13}C NMR ($CDCl_3$), δ (ppm) 98.8, 71.9, 70.3, 70.2, 66.6, 65.0, 64.9, 62.0, 58.8, 30.5, 25.4, 19.5. T_g (°C) −79.0. M_n ($\times10^5$ Da) 0.82. M_w ($\times10^5$ Da) 5.52. PDI: 6.72. Elemental analysis % calcd for C: 47.60, H: 7.93, N: 3.97; found C: 45.88, H: 8.12, N: 3.9.

Synthesis of $[(H(OCH_2CH_2)_2O)(CH_3(OCH_2CH_2)_2O)PN]_n$ (6). This polymer was synthesized using previously described deprotection conditions.[31] Compound **5** (10.0 g: 5.35 g **3**, 0.028 mol) was dissolved in 400 mL of 95% ethanol. To this solution was added a small amount of PPTS (1.0 g, 0.004 mol) to catalyze the THP deprotection reaction. This mixture was stirred at 55 °C for 4 h. After this time, the entire mixture was cooled to room temperature and transferred to dialysis tubing (6−8000 MWCO). The solution was dialyzed against

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(31) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

water for 48 h, followed by dialysis against 95% ethanol for an additional 48 h, and finally dialyzed against 100% ethanol for 72 h. The dialysis solvent reservoir was changed every 24 h. After 1 week, the clear, colorless polymer solution was removed from the dialysis bag and filtered and the solvent was removed under vacuum. The residual solid was collected and dried under high vacuum. This polymer was a clear, almost colorless gel, initially quite soluble in water and alcohols. After extended periods of time, the polymer required heating in a high boiling, polar solvent (such as dioxane, DMSO, DMF, H_2O, NMP) in order to bring about dissolution. Because of the insolubility of **6** in THF, GPC analysis was not conducted. ^{31}P NMR ($D_2O/CDCl_3$), δ (ppm) −5.94 (s). ^{1}H NMR ($D_2O/CDCl_3$), δ (ppm) 4.01 (s, 4 H); 3.56 (m, 8 H); 3.50 (s, 2 H); 3.46 (s, 2 H); 3.22 (s, 3 H). ^{13}C NMR ($D_2O/CDCl_3$), δ (ppm) 72.0, 71.3, 69.9, 69.8, 66.4, 65.7, 65.6, 60.6, 58.3. T_g (°C) −75.0. Elemental analysis % calcd for C: 40.15, H: 7.43, N: 5.20; found C: 39.18, H: 7.89, N: 5.09.

Thin-Film Preparation. The films were cast into a Teflon mold as 3/4 in. diameter disks, from a 10 wt %/vol solution of the polymer in dioxane. Polymer solutions were formulated with cross-linking agent **4** in order to yield films with approximately 50% of the side-group hydroxyl functionalities reacted. Three sets of films were cast from solution which contained 0.0, 10^{-3}, and 10^{-5} M, concentrations of **1** relative to polymer. Films made with 10^{-3} and 10^{-5} M concentrations of **1** were exposed for 72 h to an excess solution of aqueous Na_2S solution at analogous concentrations. These films were subsequently washed with water for 48 h. Films that contained no precursor were divided into two batches and were saturated over a 72 h period with either a 10^{-3} or a 10^{-5} M aqueous solution of **1**. These films were then soaked for 72 h in analogous concentrations of aqueous Na_2S. This was followed by a water wash for 48 h. In all cases, the films made with 10^{-5} M concentration of **1** were dried and embedded in epoxy resin. These samples were thin-sectioned in preparation for TEM.[32] The films made with 10^{-3} M concentration of **1** were examined with UV−vis spectroscopy.

Films Partly Cross-Linked by 10^{-3} M Solutions of 1 (System A). A solution was prepared (under argon) by dissolving **6** (1.2 g, 0.0044 mol of OH) in 12 mL of dry dioxane. To this was added **4** (0.223 g, 0.0011 mol), and the resultant solution was stirred and allowed to stand for 1 h at room temperature. After this time, 1 mL of a 1.2×10^{-5} M solution of **1** in dry DMSO was added. This mixture was stirred for an additional 15 min and was then filtered to remove any undissolved solids. The filtered solution was then cast into a mold which was used to form six 3/4 in. diameter round films. The mold was covered with a glass plate in order to allow the solvent to evaporate slowly over a period of 24 h. After this time, the films were placed in a vacuum oven and dried for an additional 24 h under vacuum at 25 °C to remove any residual solvent. The transparent, colorless films were then removed from the mold and were allowed to swell in water. The swollen films were then placed in a 1000 mL reservoir of 10^{-3} M, aqueous Na_2S, which was stirred gently for 72 h. During this time, the films did not change color noticeably They were then removed from the Na_2S solution and were soaked in distilled water for an additional 48 h. These films were used in UV−vis experiments.

Preparation of Films Partly Cross-Linked by 10^{-5} M Cross-Linked Solutions of 1 (System A). These films were prepared in a manner analogous to that described for the preparation of 10^{-3} M cross-linked films. In this case, however, 1 mL of a 1.2×10^{-7} M solution of (**1**) in dry DMSO was added to the 10% polymer−dioxane solution mixture. The films were cast and dried in a manner similar to that described above. These films were treated in a manner similar to the 10^{-3} M cross-linked films) with 10^{-4} M solution of aqueous Na_2S for 72 h, followed by washing in water for 48 h. The films were then dried under vacuum for 24 h, impregnated with epoxy resin, and prepared as thin sections in order to conduct TEM analysis.[32]

Preparation of Cross-Linked Films Infused with 10^{-3} M Solutions of 1 (System B). These films were prepared in a manner similar to that described for the preparation of 10^{-3} M cross-linked films. However, in this case no precursor (**1**) was added to the 10% polymer−dioxane solution before casting of the films. The films were cast and dried by the procedure already described. The transparent, colorless films were then removed from the mold and soaked for 72 h in a 1000 mL reservoir of 10^{-3} M aqueous solution of (**1**). These films were then soaked and stirred gently for an additional 72 h in a 1000 mL reservoir of 10^{-3} M aqueous Na_2S solution. During this time the films changed from colorless to bright yellow but were still transparent. After exposure to aqueous Na_2S, the films were washed with water for 48 h. These films were then used in UV−vis experiments.

Preparation of Cross-Linked Films Infused with 10^{-5} M Solutions of 1 (System B). These films were prepared in the same manner as described previously for the 10^{-3} M saturated films. In this case, the films were soaked in a 1000 mL reservoir of 10^{-5} M aqueous solution of **1** for 72 h and then soaked in 1000 mL of 10^{-4} M aqueous Na_2S solution for an additional 72 h. The films were then washed for 48 h in water and then dried under vacuum for 24 h. The films were then impregnated with epoxy resin and prepared as thin sections for TEM analysis.[32]

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[32] *Techniques for Electron Microscopy*; Kay, D., Ed.; Blackwell Scientific Publications: Oxford, U.K., 1961; Chapters 8−9.