

# Synthesis of a Thioether Modified Hyperbranched Polyglycerol and Its Template Effect on Fabrication of CdS and CdSe Nanoparticles

Decheng Wan, Qiang Fu, Junlian Huang

*The Key Laboratory of Molecular Engineering of Polymer, State Education Ministry of China, Department of Macromolecular Science, Fudan University, Shanghai 200433, China*

Received 6 June 2005; revised 9 September 2005; accepted 27 December 2005

DOI 10.1002/app.24202

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A thioether-containing hyperbranched polyglycerol (PG) was synthesized by a simple and effective two-step reaction; first a part of the hydroxyls of PG was transformed to carbamates by the reaction with the highly reactive 2-chloroethyl isocyanate, and then the chlorine group was *S*-alkylated with HS(CH<sub>2</sub>)<sub>*n*</sub>OH (*n* = 2, 6, 11). The resulting PGs with various molecular weights were successfully used as template for synthesis of nanoscale cadmium chalcogenide quantum dots (QDs). It was found that the size of these QDs was

dependent on the polymer template. Moreover, after solvent evaporation, the polymer was assembled into large cluster, and a variety of morphologies were formed by the cluster inside the QDs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3679–3684, 2006

**Key words:** core-shell polymer; hyperbranched; nanocomposites; templates; polyglycerol

## INTRODUCTION

Recently, inorganic quantum dot (QD) has caused much interest because of its novel properties.<sup>1–3</sup> Because most of these properties are dependent on the size and shape of the inorganic particles, the controllability of size and shape becomes important. Surfactant,<sup>4,5</sup> random ionomers,<sup>6–9</sup> and block copolymers<sup>10–13</sup> have been widely developed as the organic templates for fabrication of QDs. It is known that random ionomers and block copolymers can undergo self-organization and form microphase separated regions in bulk or selective solvents, and the size and morphology of these regions depend on the volume fraction of the respective components of the copolymer. These regions show certain affinity to inorganic species and thus can play a role as a nanoreactor. For example, Eisenberg and coworkers<sup>14</sup> showed that using polystyrene-*b*-polyacrylic acid aggregates as template for preparation of CdS, the size of the CdS depended on the absolute length of the block of polyacrylic acid.

Block copolymer has long been known to self-organize into micelle-like aggregate, although the morphology of the aggregate depended on many factors. Zhang et al.<sup>15–18</sup> showed that the relative length of polymer blocks, polymer concentration,

solvent composition, and addition of electrolyte would exert influence on the morphology of the block copolymer. Here we reported that via chemical synthesis, hyperbranched polymer can be used to construct reverse micelle-like core-shell structure conveniently. Generally speaking, the stability of this micelle-like core-shell structure should be much better than those of microdomains formed by block copolymer or ionomer, because the former is constructed by chemical bond while the latter by physical interaction. The modified hyperbranched polymer can be used as stabilizer and size controller of cadmium sulfide nanoparticle. Moreover, transmission electron micrograph proved that some large clusters were formed by polymer nanocomposite after solvent evaporation, meanwhile inside the QDs a variety of morphologies were formed by the aggregate of polymers.

## EXPERIMENTAL

### Materials

2-Chloroethyl isocyanate (98%), methanol, K<sub>2</sub>CO<sub>3</sub>, 6-mercapto-1-hexanol, acetone, 2-mercaptoethanol (99%), 1-hexanethiol (96%), 11-mercapto-1-undecanol (97%) were purchased from Aldrich or Acros and used directly, and DMF was dried by CaH<sub>2</sub>. Na<sub>2</sub>Se was purchased from Alfa. Benzoylated dialysis tubing (D-7884, MWCO 1200) was purchased from Sigma.

Correspondence to: J. Huang (jlhuang@fudan.edu.cn).

### Measurement

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on Bruker AMX 300; UV-vis spectra were recorded on a perkin-Elmer Lambda 2. FTIR were recorded on perkin-Elmer FT-IR spectrometer paragon 500. Transmission electron microscopy (TEM) analyses were carried out on a LEO 912 Omega apparatus using an acceleration voltage of 120 kV. Samples were prepared by applying a drop of the solution to a carbon-coated grid. Emission photoluminescence spectra were recorded on a Fluorolog 2 Series Spectrofluorometer.

### Synthesis of PG [(PG<sub>26</sub> (1a), PG<sub>66</sub> (1b), PG<sub>106</sub> (1c)]

PGs with different molecular weight (2000, 5000, and 8000) were synthesized in literature; the periphery hydroxyls of PG were 26, 66, and 106.<sup>19</sup>

### Synthesis of PG<sub>26</sub>-O-(2-chloroethylaminocarbonyl) (PG<sub>26</sub>-C2Cl<sub>0.59</sub>) (2a)

To a solution of 5.55 g dried **1a** in 15 mL dried DMF, 4.74 g (0.6 equiv of OH) of 2-chloroethyl isocyanate was added dropwise under atmosphere of N<sub>2</sub> and stirring. The mixture was kept at room temperature until no isocyanate group was detectable by FTIR at 2271 cm<sup>-1</sup>. After most part of DMF was removed by distillation under reduced pressure, the polymer was washed with water and dried under vacuum at 60°C to yielded 8.23 g product. **2b** (PG<sub>66</sub>C2Cl<sub>0.59</sub>) and **2c** (PG<sub>106</sub>C2Cl<sub>0.59</sub>) were synthesized similarly.  $^1\text{H}$  NMR (CD<sub>3</sub>OD):  $\delta$ /ppm, 3.30–3.50 (m, PG); 3.46 (s, —HNCH<sub>2</sub>); 3.58 (—CH<sub>2</sub>Cl), 3.5–4.40 (m, CH<sub>2</sub> of PG attached to carbamate); 4.8–5.1 (m, CH of PG attached to carbamate); 5.5–6.5 (br, —NHCO).

### Synthesis of PG<sub>26</sub>-O-carboxylaminoethylene-S-( $\omega$ -hydroxyl-hexamethylene) (PG<sub>26</sub>C2SC6OH<sub>0.59</sub>)(3c)

A mixture of **2a** (3.03 g), K<sub>2</sub>CO<sub>3</sub> (3.5 g, 1.25 equiv of Cl) in acetone (30 mL) was stirred at 60°C under N<sub>2</sub>, a solution of 6-mercapto-1-hexanol (3.6 mL) in 20 mL methanol was added slowly within 12 h, followed by stirring for another 12 h. After the inorganic salt was removed, the polymer was further purified by dialysis against methanol. 4.2 g (80%) of viscous oil was obtained.  $^1\text{H}$  NMR(CD<sub>3</sub>OD):  $\delta$ /ppm, 1.49 (—CH<sub>2</sub>CH<sub>2</sub>—CH<sub>2</sub>CH<sub>2</sub>OH); 1.50 (—CH<sub>2</sub>CH<sub>2</sub>OH); 1.63 (t, —SCH<sub>2</sub>—CH<sub>2</sub>—); 2.65 (—SCH<sub>2</sub>—); 2.71 (t, —NHCH<sub>2</sub>CH<sub>2</sub>S—); 3.39 (t, —CH<sub>2</sub>OH); 3.65 (—NHCH<sub>2</sub>); 3.5–4.40 (m, CH<sub>2</sub> of PG, including those attached to carbamate); 5.0 (m, CH of PG attached to carbamate); 4.96 (s, CH<sub>2</sub>OH).  $^{13}\text{C}$  NMR, signals independent of PG (100M, CD<sub>3</sub>OD):  $\delta$ /ppm, 26.66, 29.15, 30.93, 32.81, 33.68, 41.95, 63.01, 152.99. **3b** (PG<sub>26</sub>C2SC11OH<sub>0.59</sub>), **3d** (PG<sub>66</sub>C2SC6OH<sub>0.59</sub>), **3e** (PG<sub>106</sub>C2SC6OH<sub>0.59</sub>), **3f** (PG<sub>106</sub>C2SC6OH<sub>0.85</sub>)

were synthesized in similar method.  $^1\text{H}$  NMR of **3b** (DMSO-d<sub>6</sub>):  $\delta$ /ppm, 1.37 (—SCCH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>—COH); 1.52 (—SCH<sub>2</sub>CH<sub>2</sub>—); 1.62 (t, —CH<sub>2</sub>CH<sub>2</sub>OH); 2.65 (—SCH<sub>2</sub>—); 2.71 (t, —NHCH<sub>2</sub>CH<sub>2</sub>S—); 3.41 (t, —CH<sub>2</sub>OH); 3.65 (—NHCH<sub>2</sub>); 3.5–4.40 (m, CH<sub>2</sub> of PG including those attached to carbamate); 5.0 (m, CH of PG attached to carbamate); 4.96 (s, CH<sub>2</sub>OH).

**3a** (PG<sub>26</sub>C2SC2OH<sub>0.59</sub>) was synthesized similarly except the reaction was conducted in a mixed solvent [ethanol/acetone = 2:1(vol.)]; **3a** was water-soluble.

### Synthesis of PG<sub>26</sub>-o-carboxylaminoethylene-o-hexamethylene(pg<sub>26</sub>c2c6<sub>0.59</sub>)(3 g)

A mixture of **2a** (3.03 g), K<sub>2</sub>CO<sub>3</sub> (3.5 g, 1.25 equiv of Cl) in acetone (30 mL) was stirred at 60°C under N<sub>2</sub>, a solution of 1-hexanethiol (3.2 mL) in 20 mL acetone was added slowly within 12 h, followed by stirring for another 12 h. After the inorganic salt was removed, the polymer was further purified by dialysis against chloroform. Viscous oil (97%) was obtained.  $^1\text{H}$  NMR(CDCl<sub>3</sub>):  $\delta$ /ppm, 0.86 (t, CH<sub>3</sub>), 1.30 (—(CH<sub>2</sub>)<sub>3</sub>—CH<sub>3</sub>); 1.63 (t, —SCH<sub>2</sub>CH<sub>2</sub>—); 2.65 (—SCH<sub>2</sub>—); 2.71 (t, —NHCH<sub>2</sub>CH<sub>2</sub>S—); 3.65 (—NHCH<sub>2</sub>); 3.5–4.40 (m, CH<sub>2</sub> of PG, including those attached to carbamate); 5.0 (m, CH of PG attached to carbamate).

### Preparation of cadmium chalcogenide colloids

#### CdS colloids

A typical operation was as follows: 10 mg of **3c** was added to certain volume of a methanol solution of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (molar ratio of Cd<sup>2+</sup>/s-ether = 0.24, generally the solution was clear at such a ratio, higher ratio would lead to opaque/precipitation of the polymer solution) and the volume was adjusted to an apparent concentration of 3 mM of cadmium ion, and another freshly prepared 3 mM sodium sulfide solution in methanol was added quickly to the former under stirring at certain ratio.

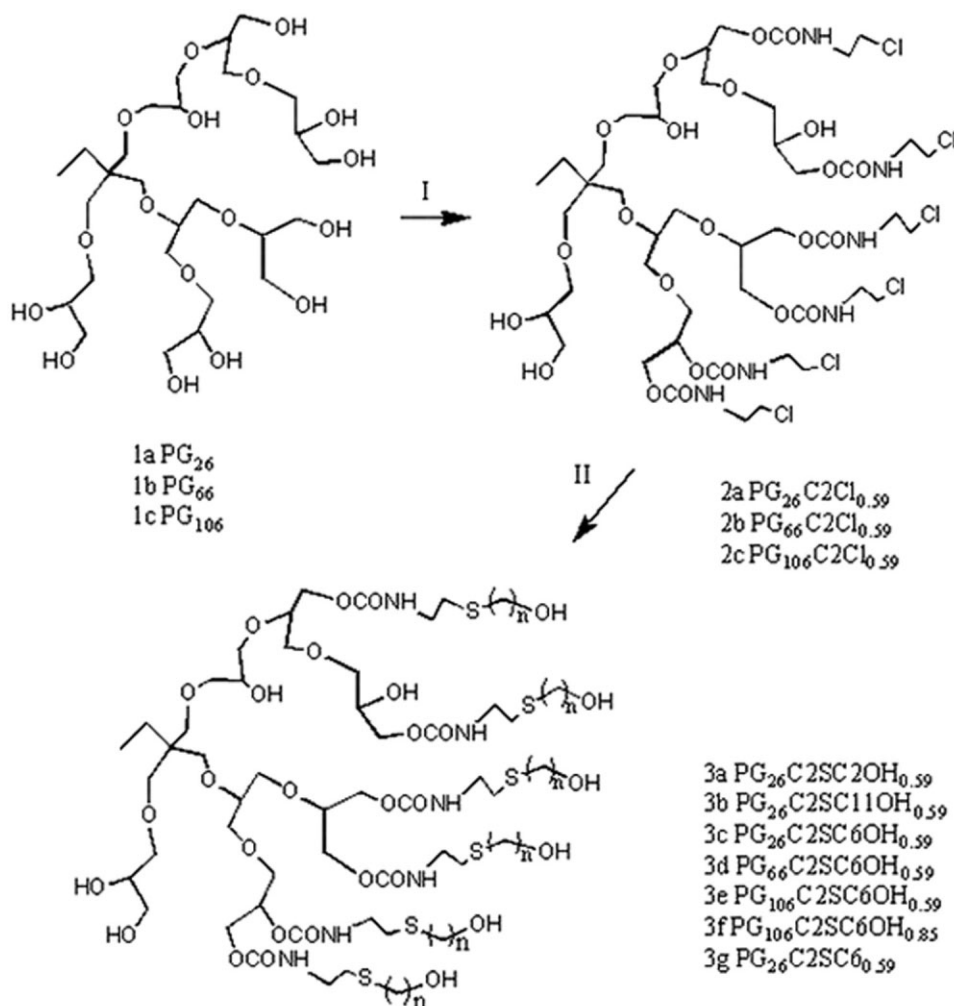
#### CdSe colloids

CdSe colloids were synthesized similarly but all operation was under N<sub>2</sub> atmosphere.

## RESULTS AND DISCUSSION

### Characterization of intermediates and object polymer

The synthesis of the target polymer is shown in Scheme 1. Hyperbranched polyglycerol (PG) was synthesized by anionic ring-opening polymerization of glycidol and adopting a slow monomer addition (SMA) technique.<sup>19</sup> The molecular weight of PG could be well controlled and the molecular weight distribu-



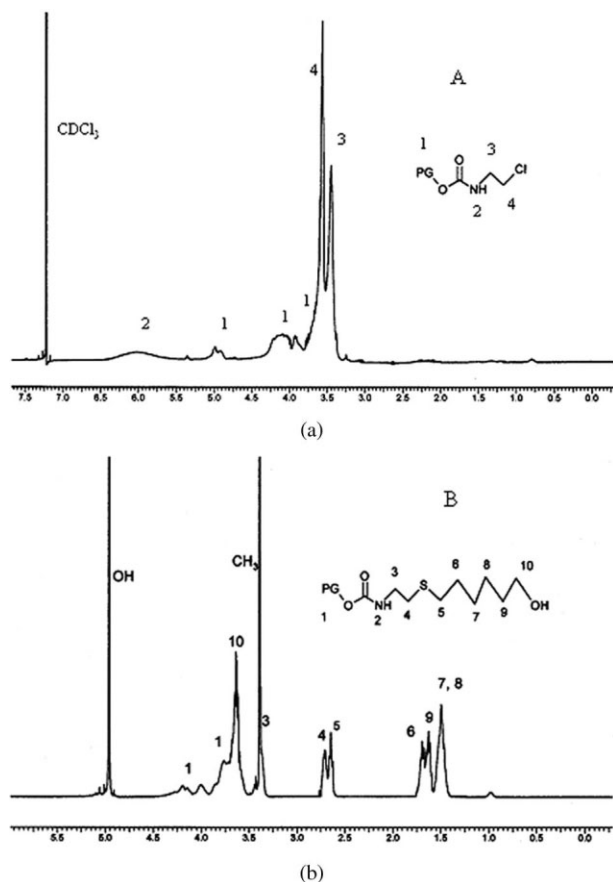
**Scheme 1** (I) 2-chloroisocyanate, DMF; (II) acetone, potassium carbonate, thiol (only 7 monomer units of PG were shown in the scheme). (Nomenclature: for example, PG<sub>26</sub>C<sub>2</sub>SC<sub>6</sub>OH<sub>0.59</sub> meant PG with 26 monomer units, and 59% of its hydroxyls was substituted by OCONH(CH<sub>2</sub>)<sub>2</sub>S(CH<sub>2</sub>)<sub>6</sub>OH).

tion was narrow. The molecular weight and molecular weight distribution of three polymers were, 2000/1.44 (1a), 5000/1.40 (1b), and 8000/1.42 (1c), respectively.

PG was first reacted with highly active 2-chloroethyl isocyanate, thus part of the hydroxyl groups were transformed into carbamate groups. Figure 1(A) showed the <sup>1</sup>H NMR spectrum of the resulted polymer. New resonance peaks at 3.46 (s, —HNCH<sub>2</sub>), 3.58(—CH<sub>2</sub>Cl), and around 6.0 ppm (NH) were observed. Additionally, partial peaks of PG were shifted to lower field after the modification; for example, the peaks at 3.2–4.0 were shifted to 3.7–4.4(m, CH<sub>2</sub> of PG attached to carbamate) and 5.0 ppm (m, CH of PG attached to carbamate). The reaction degree of PG with 2-chloroethyl isocyanate could be obtained by comparing the integrated area between 5.5 and 6.5 ppm (NH) and the overall area between 0 and 6.5 ppm. If this area ratio was *A*, then the reaction degree of PG could be calculated by: 82*A*/13.5(1 - *A*). It was found that when 0.6 equiv of isocyanate/OH was

designed in feed, practically 0.59 equiv of OH was modified, while 0.9 equiv of isocyanate/OH was designed in feed, practically 0.85 equiv of OH was modified, and that means the reaction efficiency was high.

In the further reaction, the chlorines of the aforementioned PG were further thioetherified via a highly efficient reaction with  $\alpha$ -thiol- $\omega$ -hydroxyl aliphatic hydrocarbon in the mixed solution of alcohol and acetone, and the reaction was carried out with a nearly quantitative transformation. Figure 1(B) showed the <sup>1</sup>H NMR of the reacted polymer. New resonance peaks at 1.49 (br, —CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH); 1.50 (—CH<sub>2</sub>—CH<sub>2</sub>OH); 1.63 (t, —SCH<sub>2</sub>CH<sub>2</sub>—); and 2.65 (—SCH<sub>2</sub>—) were observed. <sup>13</sup>C NMR also showed signals independent of PG (100M, CD<sub>3</sub>OD):  $\delta$ /ppm, 26.66 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.15 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 30.93 (CH<sub>2</sub>CH<sub>2</sub>OH), 32.81 (NHCH<sub>2</sub>CH<sub>2</sub>S), 33.68, (NHCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>), 41.95 (NHCH<sub>2</sub>), 63.0 (CH<sub>2</sub>OH), and 152.99(C=O).



**Figure 1**  $^1\text{H}$  NMR of **2a** in  $\text{CDCl}_3$  (A) and **3c** in  $\text{CD}_3\text{OD}$  (B).

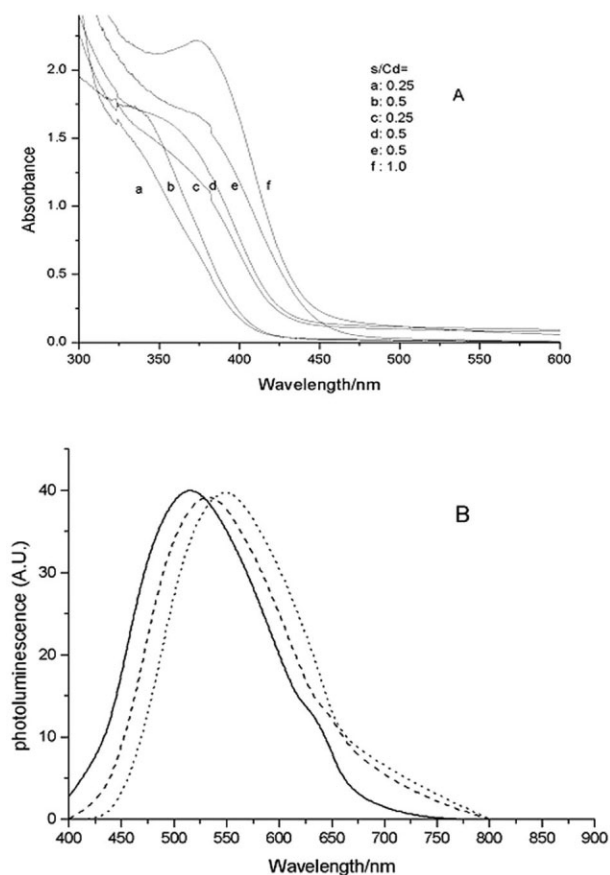
The efficiency of *S*-alkylation could also be obtained from the  $^1\text{H}$  NMR spectrum. As Figure 1(B) showed, the reaction efficiency was almost quantitative by comparing the integration area of peaks 4 and 5 (2.6–2.8 ppm) with peaks 7 and 8 (1.4–1.6 ppm). Thus, after the two-step modification, a well-defined, core-shell constructed hyperbranched polymer was obtained. To evaluate effect of the polymer template on size of the inorganic nanoparticle, PGs with molecular weight of 2000, 5000, and 8000, respectively, were employed, and all were with 59% modification degree, as shown in Scheme 1. A polymer with modification degree of 85% was also synthesized for comparison.

#### Effect of molecular weight of PG on the synthesis of CdS and CdSe colloids

To evaluate the template effect of the polymers on the size of CdS and CdSe, polymers **3c**, **3d**, and **3e** with the same thioether content and same molar ratio of cadmium ions to *S*-ether of polymer but different molecular weight were used (Scheme 1). The CdS or CdSe nanoparticles were prepared by the method of coprecipitation,<sup>20</sup> i.e., a methanol solution of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and polymer **3c** was rapidly mixed with a methanol solution of  $\text{Na}_2\text{S}$  or  $\text{Na}_2\text{Se}$  under stirring.

The effect of polymer template on size of nanoparticles could be concisely judged from band edge of UV–vis absorption spectra of semiconductors. Figure 2(A) showed that band edges of CdS mediated by polymer **3c**, **3d**, and **3e** were 406 (colorless), 426, and 441 nm (yellow), respectively. Photoluminescence [Fig. 2(B)] also showed that the spectra of CdS nanoparticle were dependent on the polymer template. These results proved that the size of CdS was polymer template dependent; in other words, the size of CdS could be somewhat controlled by the polymer template. All the data are listed in Table I.

Similarly, Figure 3 also showed that the band edges of UV–vis spectra for CdSe were 474 (greenish-yellow) mediated by **3c** and 535 nm (orange) by **3e**, respectively. We also found that for the same polymer, the variation of molar ratio of  $\text{S}^{2-}$  or  $\text{Se}^{2-}$  to  $\text{Cd}^{2+}$  did not affect the band edges.



**Figure 2** (A) UV–vis spectra of CdS nanoparticles mediated by **3c** (a, b), which was colorless, **3d** (c, d) and **3e** (e, f), which were yellow at different molar ratio of  $\text{S}^{2-}/\text{Cd}^{2+}$  in methanol; (B) emission spectra of the CdS nanoparticles mediated by **3c** (solid line), **3d** (dash line), and **3e** (dot line), which excited at 380 nm.

**TABLE I**  
Band Edges of CdS(Se) Mediated with Different Polymer Template

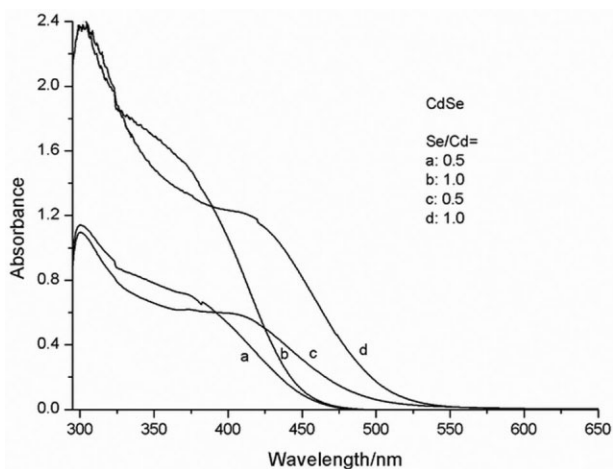
	PG <sub>x</sub> C <sub>2</sub> SC <sub>y</sub> OH <sub>z</sub> <sup>a</sup>	Band edge (nm)	
		CdS	CdSe
<b>3a</b>	PG <sub>26</sub> C <sub>2</sub> SC <sub>2</sub> OH <sub>0.59</sub>	—	—
<b>3b</b>	PG <sub>26</sub> C <sub>2</sub> SC <sub>11</sub> OH <sub>0.59</sub>	406	—
<b>3c</b>	PG <sub>26</sub> C <sub>2</sub> SC <sub>6</sub> OH <sub>0.59</sub>	406	474
<b>3d</b>	PG <sub>66</sub> C <sub>2</sub> SC <sub>6</sub> OH <sub>0.59</sub>	426	—
<b>3e</b>	PG <sub>106</sub> C <sub>2</sub> SC <sub>6</sub> OH <sub>0.59</sub>	441	535
<b>3f</b>	PG <sub>106</sub> C <sub>2</sub> SC <sub>6</sub> OH <sub>0.89</sub>	440	—
<b>3g</b>	PG <sub>26</sub> C <sub>2</sub> SC <sub>6</sub> OH <sub>0.59</sub>	404	—

See the experimental section for the synthetic conditions.

<sup>a</sup> *x*, polymerization degree of PG; *y*, carbon number of the alkyl chain of the thioether; *z*, fraction of OH group of PG that was modified.

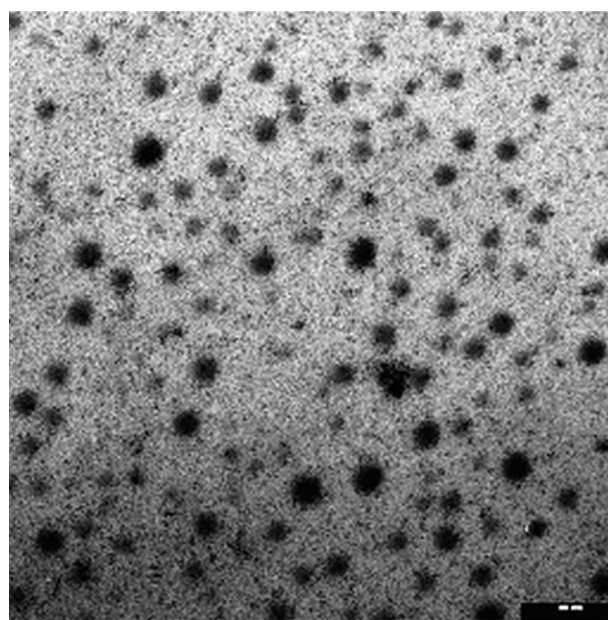
### Effect of PG with different chain length of thiols on the synthesis of CdS and CdSe colloids

Figures 2 and 3 showed that the band edges of colloidal CdS and CdSe showed little dependence on molar ratio of S<sup>2-</sup> or Se<sup>2-</sup> to Cd<sup>2+</sup>, and it means that the band edges were mainly determined by the polymer template. It was found that when the **3a**, **3b**, and **3c** with the same PG and same number of periphery hydroxyl but different chain length of thioether were mixed with cadmium nitrate, different phenomena were observed. For the **3a**, the precipitation was immediately observed even when the concentration of cadmium ions is lower, and for **3b** and **3c** no precipitates were found. The difference between polymer **3a** (PG<sub>26</sub>C<sub>2</sub>SC<sub>2</sub>OH<sub>0.59</sub>; *n* = 6), **3b** (PG<sub>26</sub>C<sub>2</sub>SC<sub>11</sub>OH<sub>0.59</sub>; *n* = 11), and **3c** (PG<sub>26</sub>C<sub>2</sub>SC<sub>6</sub>OH<sub>0.59</sub>; *n* = 6) is only the length of carbon chain of thioether; there are two methylene for **3a** and eleven and six for **3b** and **3c**,

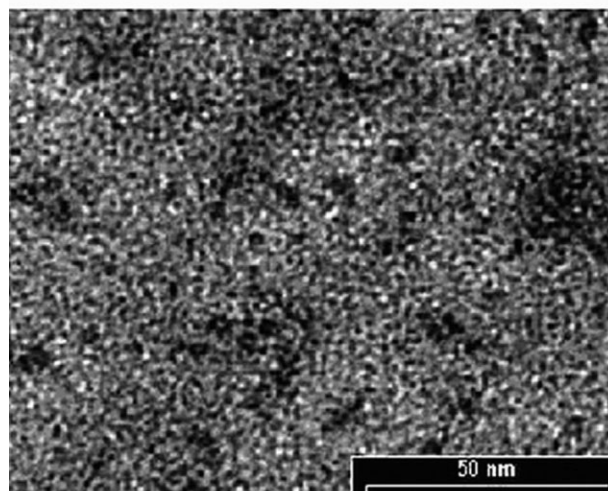


**Figure 3** UV-vis spectra of CdSe nanoparticles mediated by **3c** (a,b, greenish-yellow) and **3e** (c,d, orange) at different molar ratio of Se<sup>2-</sup>/Cd<sup>2+</sup> in methanol; the band edge was 474 and 535 nm, respectively.

respectively. The formation of precipitate when the **3a** was mixed with cadmium nitrate may attribute to the interpolymer crosslinking by the coordinate interaction between cadmium ion and thioether or carbamate, which means that the cadmium ions shared much high affinity to thioether or carbamate group when the length of carbon chain of thioether is shorter. For other polymers such as **3b** and **3c**, however, no precipitation of the polymers were observed when they were mixed with cadmium ions; the long carbon chains of polymers **3b** (eleven methylene groups) and **3c** (six methylene groups) may prevent the coordination between cadmium ions and thioethers or carbam-



**A**



**B**

**Figure 4** TEM micrograph. (A) The spherical particles were cluster of polymer **3e** (scale bar: 200 nm); (B) amplification of part of micrograph (A), which showed the smaller CdSe dots inside the polymer cluster (scale bar: 50 nm).

ate to form the intermolecular crosslinking. That is why cadmium ions colloids mediated with **3b** and **3c** are clear, and no difference on band edges in UV-vis spectra was observed. However, when the molecular weight of PG was varied (**3c**, **3d**, **3e**), the band edges were also changed, and so we think the size of the nanoparticles was mainly dependent on the molecular weight of PG and independent on the length of carbon chain of thioether.

Transmission electron microscopy (TEM) was also employed to characterize the particles. Figure 4 showed TEM micrograph of CdSe colloids mediated by **3e**, and the image was taken when the solvent methanol was evaporated. Strangely, the micrograph (A) showed particles with average diameter of 43 nm, and these particles could not be CdSe, because the band edge of 535 nm (Fig. 3) corresponded to CdSe with diameter of 2.7 nm.<sup>21</sup> The particles were most probably the cluster of polymers **3e**, and the formation of these clusters was related to the hydroxyls on surface of the polymers. To confirm it, polymer **3g** without hydroxyls in toluene was used to substitute **3e**, and no clusters were observed after the evaporation of toluene. Additionally, from the amplified micrograph [Fig. 4(B)], it could be found that there were darker black dots distributed through the cluster and these black dots were CdSe particles. Some black dots outside the polymer cluster should be sodium nitrate produced during the preparation of CdSe. Besides dots, there were a variety of morphologies such as pots, strung pearls, and networks of CdSe in the polymer cluster. These rich transition structures were formed during the evaporation of methanol; the mechanism have recently been exploited and the structure has been predicted by simulation.<sup>22</sup>

## CONCLUSIONS

Thioether-containing hyperbranched polyglycerol could be used to mediate CdS and CdSe nanoparticles;

the size of these inorganic particles was depended on the size of the hyperbranched polyglycerol. Additionally, the hydroxyl groups on the surface of the polymer could drive the polymer self-assembly into clusters, while the CdS or CdSe in the cluster formed a variety of transition structures during solvent evaporation.

## References

1. Han, M. Y.; Gao, X. H.; Su, J. Z.; Nie, S. M. *Nat Biotechnol* 2001, 19, 631.
2. Chan, W. C. W.; Nie, S. M. *Science* 1998, 281, 2016.
3. Pathak, S.; Choi, S. K.; Arnheim, N.; Thompson, M. E. *J Am Chem Soc* 2001, 123, 4103.
4. Pileni, M. P.; Motte, L.; Petit, C. *Chem Mater* 1992, 4, 338.
5. Watzke, H. J.; Fendler, J. H. *J Phys Chem* 1987, 91, 854.
6. Krishnan, M.; White, J. R.; Fox, M. A.; Bard, A. J. *J Am Chem Soc* 1983, 105, 7002.
7. Mau, A. W.-A.; Huang, C. B.; Kakuta, N.; Bard, A. J.; Campion, A.; Fox, M. A.; White, J. M.; Webber, S. E. *J Am Chem Soc* 1984, 106, 6537.
8. Hilinski, E. F.; Lucas, P. A.; Wang, Y. *J Chem Phys* 1988, 89, 3435.
9. Wang, Y.; Suna, A.; Mahler, W.; Kasowski, R. *J Chem Phys* 1987, 87, 7315.
10. Cummins, C. C.; Schrock, R. R.; Cohen, R. E. *Chem Mater* 1992, 4, 27.
11. Yue, J.; Sankaran, V.; Cohen, R. E.; Schrock, R. R. *J Am Chem Soc* 1993, 115, 4409.
12. Ng Cheong Chan, Y.; Craig, G. S. W.; Schrock, R. R.; Cohen, R. E. *Chem Mater* 1992, 4, 885.
13. Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *J Am Chem Soc* 1992, 114, 7295.
14. Moffitt, M.; McMahon, L.; Pessel, V.; Eisenberg, A. *Chem Mater* 1995, 7, 1185.
15. Zhang, L.; Eisenberg, A. *Science* 1995, 268, 1728.
16. Zhang, L.; Eisenberg, A. *J Am Chem Soc* 1996, 118, 3168.
17. Zhang, L.; Yu, K.; Eisenberg, A. *Science* 1996, 272, 1777.
18. Zhang, L.; Eisenberg, A. *Macromolecules* 1996, 29, 8805.
19. Sunder, A.; Hanselmann, H.; Frey, H.; Mülhaupt, R. *Macromolecules* 1999, 32, 4240.
20. Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J Am Chem Soc* 1987, 109, 5649.
21. Peng, X. G.; Wickman, J.; Alivisatos, A. P. *J Am Chem Soc* 1998, 120, 5343.
22. Rabani, E.; Reichman, D. R.; Geissler, P. L.; Brus, L. E. *Nature* 2003, 426, 271.