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Synthesis of Monodisperse CdS Nanospheres in an Inverse Microemulsion System Formed with a Dendritic Polyether Copolymer

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Nanosized CdS spheres with diameters of about 25, 40, and 50 nm have been synthesized in three inverse microemulsions formed with a dendritic amphiphilic copolymer (H_2O/SD31/*n*-butanol/*n*-heptane) through the reaction of cadmium chloride ($CdCl_2$) with the S^{2-} ions that were slowly released from thioacetamide (TAA). X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and UV/Vis absorption and photoluminescence (PL) spectroscopy were used to characterize the CdS nanospheres obtained. TEM and XRD studies showed that monodisperse CdS nanospheres with the zinc blende structure were produced, and the size of the CdS spheres increased with increasing water-core size because of the increasing [water]/[dendrimer] mass ratio (ω). The blueshift of the maxima in the UV/Vis absorption and PL spectra indicated that the CdS spheres consisted of primary CdS nanocrystals showing a quantum confinement effect. The viscosities of the three microemulsions were also determined by rheological measurements. The viscosity of the inverse microemulsion system decreased as ω increased. The water core of the inverse microemulsion provided a soft template for the precipitation of CdS spheres.

Introduction

Nanocrystals have attracted broad attention from researchers in various disciplines.[1] They exhibit size-dependent characteristics and often display novel electronic, magnetic, optical, chemical, and mechanical properties that cannot be obtained in their bulk counterparts. Among the various nanocrystals, semiconductor nanocrystals, represented by Group II–IV nanocrystals with either zinc blende or wurtzite structures, have been the most studied because of their nonlinear optical and luminescence properties, quantum size effect, and other important physical and chemical features.[2,3] Altering the size of the particles changes the degree of the confinement of the electrons and affects the electronic structure of the solid, especially the bandgap edges, which can be tuned by varying the particle size. Chalcogenides such as CdS,[4–14] ZnS,[15–21] HgS,[22–24] PdS,[25–29] and MnS,[30,31] have been intensively investigated. Among these inorganic nanoparticles, CdS nanoparticles have received great attention. CdS, as an important Group II–IV semiconductor compound with a wide bandgap (energy = 2.53 eV), has attracted much research interest due to its excellent properties of luminescence and photochemistry.

To date, various methods have been developed to synthesize nanoparticles of CdS semiconductors. Recently, solvothermal or hydrothermal methods,[32] evaporation processes,[33] mesoporous silica and monoliths,[34] and sol–gel methods[35] have been utilized to prepare CdS. Other methods involve arrested precipitation from simple inorganic ions using polyphosphate and low-molecular-weight thiols as stabilizers.[36–38] Surfactants,[39] block copolymers,[40] and dendrimers[41] have also been used as specific stabilizers and soft templates for the synthesis of CdS nanoparticles in solution. However, water-in-oil microemulsions with nanometer-sized water cores are well-suited for nanoparticles. As the method that uses such microemulsions works in mild and normal environments, it is advantageous and considered to have good viability. No special conditions of pressure, irradiation, etc. are required.[42] Many kinds of CdS nanoparticles have been synthesized by this method.[43] The nanowater core acts as a nanoreactor, and the size of the prepared nanoparticles can be controlled.[44]

In previous studies, microemulsions were generally composed of low-molecular-weight surfactants. However, amphiphilic macromolecules, in particular amphiphilic dendrimers, can also be used to prepare microemulsions. Dendrimers are defined as macromolecules containing highly branched and dimensional structures with a large number of reactive terminal groups.[45] Water-soluble amphiphilic dendrimers have attracted considerable attention due to their unique properties and as new polymeric materials for applications in many areas such as the preparation of micelles, liquid crystals, microemulsions, and molecular encapsulation.[46,47] The synthesis of an amphiphilic dendritic polyether copolymer and its demulsification on crude oil were studied in our previous work.[48]

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In this article, we prepared water-in-oil microemulsions with an amphiphilic dendritic polyether copolymer SD31 as a microreactor to synthesize CdS nanoparticles and tested the feasibility of this method. As a result, nanosized monodisperse CdS spheres with diameters of 25–50 nm were obtained. The dimension of the CdS nanospheres encapsulated in microemulsion droplets could be controlled by varying the water-core size, i.e., varying the [water]/[dendrimer] mass ratio (ω). The effects of the variation of ω on the synthesis were carefully examined and found to shed light on the mechanism of formation.

Results and Discussion

Typical TEM images of CdS spheres with different sizes obtained in three different microemulsions are presented in Figure 1, which shows that the shape of all the products is spherical. However, the size is varied. The diameter of the spheres synthesized in microemulsion A is around 25 nm (Figure 1a and b), while the sphere diameters of other two samples synthesized in microemulsions B and C are about 40 and 50 nm, respectively (Figure 1c and d, e and f). It could be concluded that the size of the products increased as the [water]/[dendrimer] mass ratio (ω) increased. The size of w/o microemulsion droplets is highly dependent on the concentration of each constituent in the microemulsion. However, it is recognized that the water-core size is dominantly characterized by the [water]/[surfactant] ratio, rather than the actual concentration. The radius of the water core is found to follow an approximately linear relationship with the [water]/[surfactant] ratio,[49] because the size of the water core of the microemulsion increases as ω increases. The larger water core acts as a nanoreactor that induces larger particle growth.[50] These properties and their reasons are discussed in detail below.

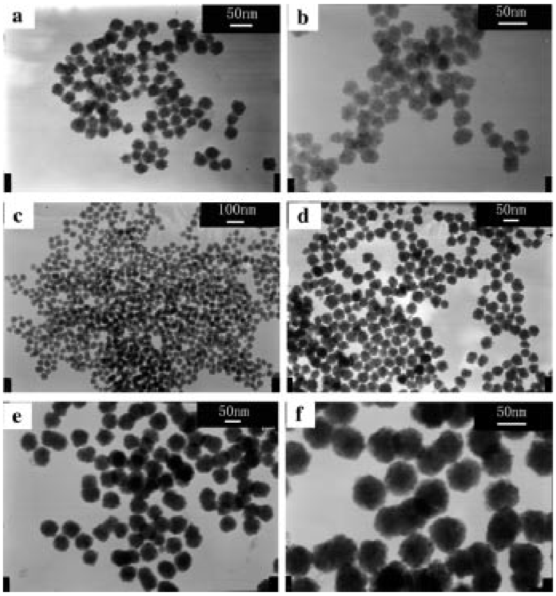


Figure 1. TEM images of CdS spheres obtained in three microemulsions with different [water]/[dendrimer] mass ratios (ω): (a and b) products from microemulsion A (ω = 0.19); (c and d) products from microemulsion B (ω = 0.21); (e and f) products from microemulsion C (ω = 0.24).

The wide-angle XRD patterns for the CdS nanospheres prepared in the three microemulsions are shown in Figure 2. Diffraction peaks assigned to the (111), (200), (220), and (311) planes of bulk cubic CdS are observed for samples produced from microemulsions B and C. For the smallest sample produced from microemulsion A, the diffraction peaks are not obvious except for that of the (111) plane, which indicates incomplete crystallization of CdS and lattice defects. The diffraction peaks are fairly broad. We estimated roughly the average crystallite sizes of the primary particles by line-width analysis of the (111) diffraction peaks. Applying the Scherrer formula yielded particle sizes of 1.2, 1.6, and 2.7 nm for syntheses carried out in microemulsions A, B, and C, respectively.

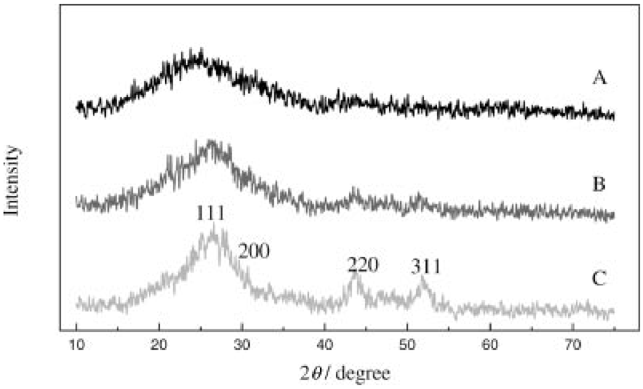


Figure 2. XRD patterns of CdS spheres obtained in the three microemulsion systems.

Figure 3 shows the intensities and wavelengths of the UV/Vis absorption peaks of the CdS spheres at various times during the process of formation. After addition of TAA, the mixture was kept at constant temperature (50 °C), and UV/Vis spectra were recorded at various time intervals. In the beginning, the solution was colorless, and there was no obvious peak in the absorption spectrum. After 30 min, the solution became slightly yellow, and an absorption peak appeared in the spectrum along with a considerable increase in absorbance. In Figure 3a, curves A′, B′, and C′ show that the absorption intensity increased with time, indicating a gradual formation of CdS particles accompanying the release of S^{2-} ions from TAA. However, the position of the absorption peak was different in the three systems (Figure 3a, curves A, B, and C). The absorption peak of CdS synthesized in microemulsion A was at about 420 nm and the peak was obvious and sharp. With increasing time, the wavelength of the absorption peak remained essentially unchanged, even though the absorption intensity increased continuously, suggesting the formation of more and more CdS particles and the possible presence of large aggregates of the primary CdS particles, but the size of the primary CdS particles remained unchanged. The absorption of CdS obtained in microemulsion B displayed a shoulder peak close to 410 nm, and the absorption band of CdS obtained in microemulsion C was at wavelengths no longer than about 390 nm in the beginning. Curves B and C (Figure 3a) show that the absorption peaks continuously shifted towards higher wavelengths upon further heating of the solutions. This red-shifting phenomenon indicates that the primary CdS particles grew gradually and then aggregated to form larger particles due to the quantum confinement effect. From the changes in the UV/Vis spectra of the three microemulsions, it can be deduced that the mechanism of formation of the CdS spheres was different in each system. In microemulsion A, once the CdS particles nucleated, the particles ceased growing, but more CdS particles formed or aggregated. In microemulsions B and C, although the CdS particles initially nucleated were smaller than those in microemulsion A, the primary particles grew gradually and also aggregated to form larger particles.

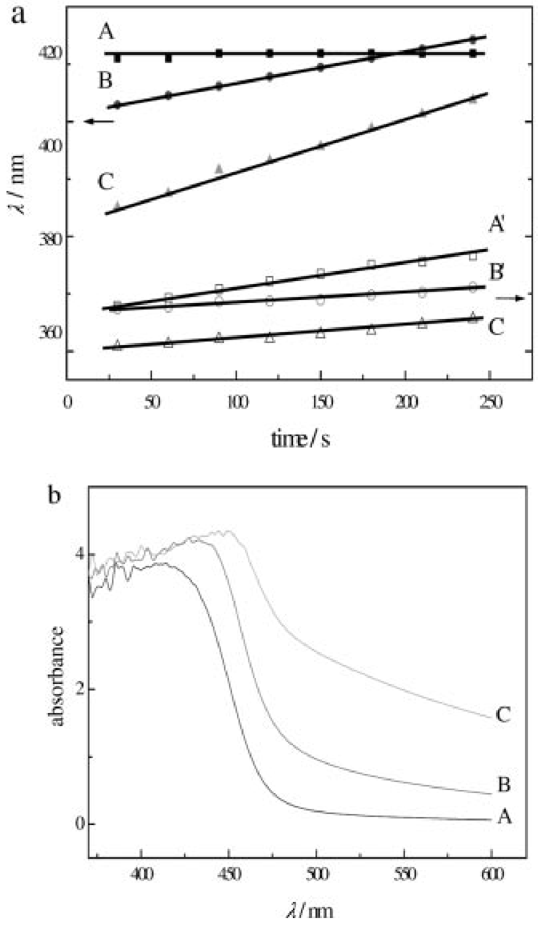


Figure 3. (a) Graphs of the wavelengths and intensities of the UV/Vis absorption peaks of the CdS products formed in the three microemulsions at earlier stages: curves A, B, and C show wavelength vs. time; curves A′, B′, and C′ show intensity vs. time. (b) UV/Vis absorption spectra of the final CdS products in the three microemulsions after eight hours. A and A′ represent microemulsion A ($\omega = 0.19$); B and B′ represent microemulsion B ($\omega = 0.21$); C and C′ represent microemulsion C ($\omega = 0.24$).

Figure 3b shows the UV/Vis absorption spectra of the CdS products in the three microemulsions after eight hours. As shown in Figure 3b, the absorption spectra of the final products have peaks at 420 (microemulsion A), 440 (microemulsion B), and 450 nm (microemulsion C), which are all considerably blue-shifted relative to the absorption onset of bulk CdS (ca. 515 nm) because of the quantum confinement effect. It was interesting that CdS particles in microemulsions B and C were larger than those in microemulsion A in the end, so that the wavelength of the absorption maximum increased from A to C. The absorption peaks of B and C are obviously red-shifted relative to their initial positions, indicating the growth of the primary particles. The spectra of B and C also show a long absorption tail due to scattering by the particles in the dispersion. The absorption intensity increased with increasing particle size because of light scattering in the presence of bigger particles. From the experimental correlation between the onset of absorption and the particle diameter for CdS, the particle size of CdS nanocrystals was estimated to be about 2–3 nm and to increase from A to C.[36] These values follow the same trend as the results of XRD, which exhibit a quantum confinement effect.

The PL spectra of the CdS spheres are shown in Figure 4. The broad emission beginning around 430 nm is significantly blue-shifted from the emission of bulk CdS (ca. 520 nm). The broad PL peak observed is commonly attributed to the recombination of charged carriers trapped in the surface states and is related to the size of the CdS nanoparticles; that is, the PL bands of smaller nanoparticles appear at shorter wavelengths. Therefore, the PL emission of the CdS spheres indicates that they actually consist of primary CdS nanocrystals showing a quantum confinement effect.

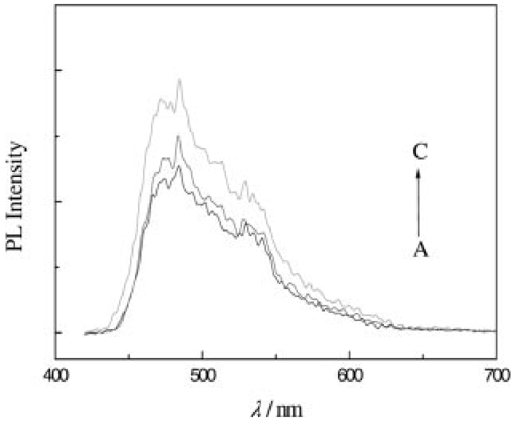


Figure 4. Photoluminescence spectra of CdS spheres obtained in three microemulsions after 8 h ($\lambda_{ex} = 400$ nm).

Figure 5, which shows the stress at different shear rates, depicts the key results from steady-shear rheological measurements. During the experiments of shear rates, the three microemulsion systems were all Newtonian fluids. The relatively high viscosity was due to amphiphilic dendrimer content. It can be seen that shear stress increased as shear rate increased. In addition, the viscosity of the three microemulsions decreased with increased [water]/[dendrimer] mass ratio (ω). This property of the microemulsion can be used to explain the different size of the products. High viscosity led to low ion flow and ion exchange, which affected the growth of CdS particles in the water core and further reduced the possibility of large aggregates of the primary CdS particles. The larger particles were obtained for microemulsion C with lower viscosity. This result is consistent with the observations of the TEM images and the UV/Vis absorption spectra.

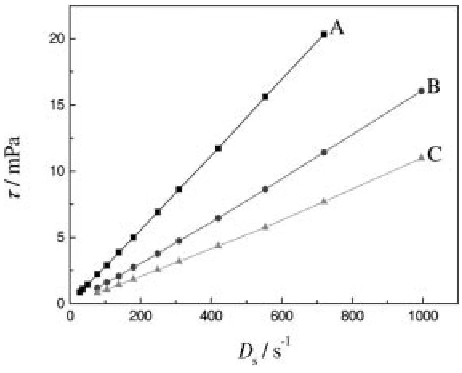
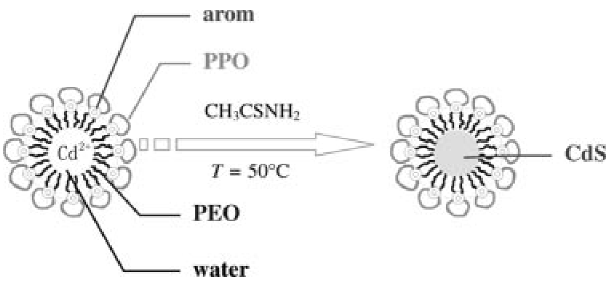


Figure 5. Shear stress vs. shear rate curves for the three microemulsion systems without CdS particles. (A) microemulsion A (ω = 0.19), (B) microemulsion B (ω = 0.21), (C) microemulsion C (ω = 0.24).

On the basis of the above observations and the monodisperse nanosphere structure we were able to propose a possible mechanism, as shown in Scheme 1. In the inverse microemulsion H_2O/SD31/*n*-butanol/*n*-heptane, the hydrophilic PEO of the amphiphilic dendritic polyether copolymer SD31 formed the water core, and the hydrophobic PPO and arom parts were oriented outwards. The cadmium ions that were initially dissolved in the water core reacted with the S^{2-} ions that were slowly released from thioacetamide (TAA). Monodisperse CdS nanospheres were obtained because the reaction was restricted to the nanowater core.



Scheme 1. Proposed mechanism for the formation of monodisperse CdS nanospheres; PEO = poly(ethylene oxide), PPO = poly(propylene oxide), arom = bisphenol A.[48]

Conclusions

Nanosized CdS spheres were facilely synthesized in water-in-oil microemulsions prepared by amphiphilic dendrimers through the slow release of S^{2-} ions from thioacetamide under heating. It was shown that the nanometer-sized water cores are well-suited for nanoparticle synthesis. Particle growth occurs within the water core of the microemulsion, and the precursors of the semiconductor particles are water-soluble. The sizes of the CdS spheres obtained in three different systems are diverse, but all spheres are composed of cubic CdS crystals of the zinc blende structure. It was revealed that the diameter of the CdS spheres increased as the [water]/[dendrimer] mass ratio (ω) increased, i.e., as the water-core size increased. The viscosity of the three microemulsions decreased with increased ω, which affected the flow and exchange of the ions. High viscosity led to low ion flow and induced small particles to form, preventing the particles from aggregating. It is expected that this convenient synthetic route to CdS spheres may be readily extended to the fabrication of other metal chalcogenide semiconductor nanoparticles.

Experimental Section

Materials: Unless otherwise noted, all chemicals were reagent grade and were used as received without purification. Amphiphilic dendritic polyether copolymer SD31 (MW = 10600 g mol^{-1}) was synthesized as per ref.[48] and the molecular structure is shown schematically in Figure 6. Thrice distilled water was used in all experiments.

Determination of the Phase Diagram: The quasiternary phase diagram was constructed at room temperature (25 ± 1 °C). SD31 and the cosurfactant, *n*-butanol, were combined in the mass ratio1:2. Then *n*-heptane was combined with the above mixture in the mass ratios 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 and shaken vigorously. Water was gradually added dropwise to the above 10 samples under shaking, and then the samples were left to settle for two days. The formation of water-in-oil microemulsions was determined through visual observation, which revealed the phase transformation or phase separation of the ternary system. The quasiternary phase diagrams of the systems are given in Figure 7.

Synthesis of CdS Nanoparticles: In the water-in-oil microemulsion region, three systems (see Figure 7 A, B, and C) with the same amount of water (6% wt.) but different [water]/[dendrimer] mass ratios (ω) were selected as nanometer-sized reaction cores to synthesize CdS. In a typical experiment, microemulsion A, containing $CdCl_2$ solution (1.44 mL, 0.1 M), dendrimer SD31 (7.5 g), and *n*-butanol (15 g), was prepared. Thioacetamide (TAA) solution (1.44 mL, 0.1 M in ethanol) was added to microemulsion A whilst stirring until a homogeneous mixture formed. Then the final microemulsion was sealed and placed under constant temperature (50 °C) for 8 h, where the slow release of S^{2-} ions from TAA led to the formation of CdS particles. The resulting solution was centrifuged at 12000 rmp, washed with ethanol under sonication, and separated by repeated centrifugation. The final product was dried to yield a powder at 50 °C. Microemulsion B was composed of $CdCl_2$ (1.60 mL, 0.1 M), dendrimer SD31 (7.5 g), *n*-butanol (15 g), and *n*-heptane (2.5 g), while microemulsion C was composed of $CdCl_2$ (1.68 mL, 0.1 M), dendrimer SD31 (7 g), *n*-butanol (14 g), and *n*-heptane (5.3 g).

Characterization: Transmission electron microscopy (TEM, JEM100-CXII) was used to directly observe the morphology and size of products. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku D/Max 2200-PC diffractometer with Cu-K_α radiation (λ = 1.5418 Å) and a graphite monochromator at ambient temperature. UV/Vis absorption spectra were obtained with

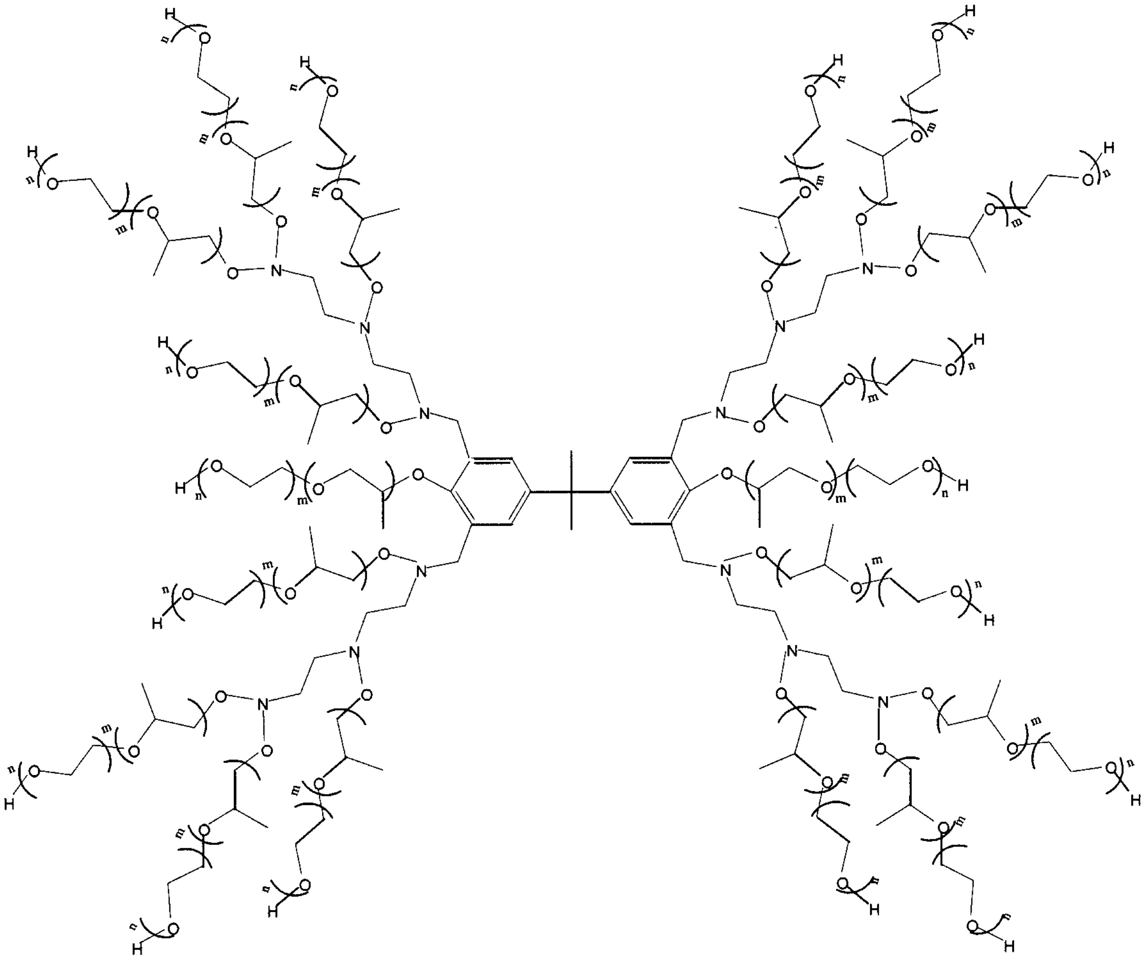


Figure 6. The molecular structure of the amphiphilic dendrimer SD31.

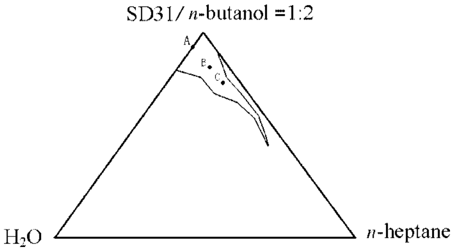


Figure 7. Ternary phase diagram of the H_2O/SD31/n-butanol/n-heptane system. Inset shows the water-in-oil (w/o) inverse microemulsion region. A (ω = 0.19), B (ω = 0.21), and C (ω = 0.24) were the three microemulsions used in nanoparticle synthesis.

a Hitachi U-4100 dual-beam grating spectrophotometer with a 10-mm quartz cell. PL spectra were obtained with a Perkin-Elmer LS-55 fluorescence spectrophotometer. The excitation wavelength λ_{ex} was 400 nm, and the bandwidths of excitation and emission were both 10 nm. Fluorescence measurements were obtained on suspensions in quartz cuvettes. Shear stress versus shear rate rheological data was measured with an NXS-11A rotary viscometer.

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[1] a) K. J. Klabunde, *Nanoscale Materials in Chemistry*, Wiley-Interscience, New York, **2001**; b) J. H. Fendler, *Nanoparticles and Nanostructured Films*, Wiley-VCH, Weinheim, Germany, **1998**; c) A. L. Rogach, D. V. Talapin, E. V. Shevchenko, A. Kornowski, M. Haase, H. Weller, *Adv. Funct. Mater.* **2002**, *12*, 653–664.

[2] J. Joo, H. B. Na, T. Yu, J. H. Yu, Y. W. Kim, F. Wu, J. Z. Zhang, T. Hyeon, *J. Am. Chem. Soc.* **2003**, *125*, 11100.

[3] W. Wang, I. Germanenko, M. S. El-Shall, *Chem. Mater.* **2002**, *14*, 3028–3033.

[4] T. F. Towey, A. Khan-Lodi, B. H. Robinson, *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3757–3762.

[5] a) T. Trindade, P. O'Brien, X. Zhang, *Chem. Mater.* **1997**, *9*, 523–530; b) C. S. Yang, D. D. Awschalom, G. D. Stucky, *Chem. Mater.* **2001**, *13*, 594–598; c) H. Zhao, E. P. Douglas, *Chem. Mater.* **2002**, *14*, 1418–1423.

[6] a) R. Rossetti, R. Hull, J. M. Gibson, L. E. Brus, *J. Chem. Phys.* **1985**, *82*, 552–559; b) R. Rossetti, J. L. Ellison, J. M. Gibson, L. E. Brus, *J. Chem. Phys.* **1984**, *80*, 4464–4469.

[7] M. Ohtaki, K. Oda, K. Eguchi, H. Arai, *Chem. Commun.* **1996**, 1209–1210.

[8] a) C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715; b) C. J. Barrelet, Y. Wu, D. C. Bell, C. M. Lieber, *J. Am. Chem. Soc.* **2003**, *125*, 11498–11499; c) Y. C. Cao, J. Wang, *J. Am. Chem. Soc.* **2004**, *126*, 14336–14337.

[9] a) T. Torimoto, H. Kontani, Y. Shibutani, S. Kuwabata, T. Sakata, H. Mori, H. Yoneyama, *J. Phys. Chem. B* **2001**, *105*, 6838–6845; b) L. F. Dong, T. Gushtyuk, J. Jiao, *J. Phys. Chem. B*

2004, *108*, 1617–1620; c) T. Gao, T. H. Wang, *J. Phys. Chem. B* **2004**, *108*, 20045–20049.

[10] a) H. Y. Zhao, E. P. Douglas, B. S. Harrison, K. S. Schanze, *Langmuir* **2001**, *17*, 8428–8433; b) Y. J. Hsu, S. Y. Lu, *Langmuir* **2004**, *20*, 23–26.

[11] X. J. Zhang, Q. R. Zhao, Y. P. Tian, Y. Xie, *Cryst. Growth Des.* **2004**, *4*, 355–359.

[12] D. Dorfs, A. Eychmuller, *Nano Lett.* **2001**, *1*, 663–665.

[13] T. J. Boyle, S. D. Bunge, T. M. Alam, G. P. Holland, T. J. Headley, G. Avilucea, *Inorg. Chem.* **2005**, *44*, 1309–1318.

[14] U. S. Jeng, Y. S. Sun, H. Y. Lee, C. H. Hsu, K. S. Liang, S. W. Yeh, K. H. Wei, *Macromolecules* **2004**, *37*, 4617–4622.

[15] X. Li, J. R. Fryer, D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.* **1994**, 1715–1716.

[16] a) V. Sankaran, J. Yue, R. E. Cohen, R. R. Schrock, R. J. Silbey, *Chem. Mater.* **1993**, *5*, 1133–1142; b) M. R. Knecht, D. W. Wright, *Chem. Mater.* **2004**, *16*, 4890–4895.

[17] a) R. K. Rana, L. Zhang, J. C. Yu, Y. Mastai, A. Gedanken, *Langmuir* **2003**, *19*, 5904–5911; b) Y. R. Ma, L. M. Qi, J. M. Ma, H. M. Cheng, *Langmuir* **2003**, *19*, 4040–4042.

[18] L. S. Li, N. Pradhan, Y. J. Wang, X. G. Peng, *Nano Lett.* **2004**, *4*, 2261–2264.

[19] X. Chen, H. Xu, N. Xu, F. Zhao, W. Lin, G. Lin, Y. Fu, Z. Huang, H. Wang, M. Wu, *Inorg. Chem.* **2003**, *42*, 3100–3106.

[20] D. F. Moore, Y. Ding, Z. L. Wang, *J. Am. Chem. Soc.* **2004**, *126*, 14372–14373.

[21] P. Hu, Y. Liu, L. Fu, L. Cao, D. Zhu, *J. Phys. Chem. B* **2004**, *108*, 936–938.

[22] K. A. Higginson, M. Kuno, J. Bonevich, S. B. Qadri, M. Yousuf, H. Mattoussi, *J. Phys. Chem. B* **2002**, *106*, 9982–9985.

[23] B. Pal, S. Ikeda, B. Ohtani, *Inorg. Chem.* **2003**, *42*, 1518–1524.

[24] X. Chen, X. Wang, Z. Wang, X. Yang, Y. Qian, *Cryst. Growth Des.* **2005**, *5*, 347–350.

[25] Y. Wang, N. Herron, *J. Phys. Chem.* **1987**, *91*, 257–260.

[26] a) M. Moffitt, A. Eisenberg, *Chem. Mater.* **1995**, *7*, 1178–1184; b) R. Tassoni, R. R. Schrock, *Chem. Mater.* **1994**, *6*, 744–749.

[27] S. Gallardo, M. Gutierrez, A. Henglein, E. Janata, *Ber. Bunsenges. Phys. Chem.* **1989**, *93*, 1080–1090.

[28] F. Gao, Q. Lu, X. Liu, Y. Yan, D. Zhao, *Nano Lett.* **2001**, *1*, 743–748.

[29] A. Berman, N. Belman, Y. Golan, *Langmuir* **2003**, *19*, 10962–10966.

[30] J. Lu, P. F. Qi, Y. Y. Peng, Z. Y. Meng, Z. P. Yang, W. C. Yu, Y. T. Qian, *Chem. Mater.* **2001**, *13*, 2169–2172.

[31] Y. W. Jun, Y. Y. Jung, J. Cheon, *J. Am. Chem. Soc.* **2002**, *124*, 615–619.

[32] a) J. Yang, J.-H. Zeng, S.-H. Yu, L. Yang, G.-E. Zhou, Y.-T. Qian, *Chem. Mater.* **2000**, *12*, 3259–3263; b) P. Zhang, L. Gao, *Langmuir* **2003**, *19*, 208–210.

[33] a) C. Ye, G. Meng, Y. Wang, Z. Jiang, L. Zhang, *J. Phys. Chem. B.* **2002**, *106*, 10338–10341; b) G. Shen, C.-J. Lee, *Cryst. Growth Des.* **2005**, *5*, 1085–1089; c) J. Zhang, F. Jiang, L. Zhang, *J. Phys. Chem. B.* **2004**, *108*, 7002–7005.

[34] a) S. Besson, T. Gacoin, C. Ricolleau, C. Jacquiod, J.-P. Boilot, *Nano Lett.* **2002**, *2*, 409–414; b) W. Xu, Y. Liao, D. L. Akins, *J. Phys. Chem. B.* **2002**, *106*, 11127–11131; c) C. Tura, N. Coombs, O. Dag, *Chem. Mater.* **2005**, *17*, 573–579; d) Z. Zhang, S. Dai, X. Fan, D. A. Blom, S. J. Pennycook, Y. Wei, *J. Phys. Chem. B.* **2001**, *105*, 6755–6758.

[35] a) P. Xue, R. Lu, Y. Huang, M. Jin, C. Tan, C. Bao, Z. Wang, Y. Zhao, *Langmuir* **2004**, *20*, 6470–6475; b) T. Gacoin, K. Lahlil, P. Larregaray, J.-P. Boilot, *J. Phys. Chem. B.* **2001**, *105*, 10228–10235.

[36] T. Vossmeyer, L. Katsikas, M. Giersig, I. G. Popovic, K. Diesner, A. Chemseddine, A. Eychmüller, H. Weller, *J. Phys. Chem.* **1994**, *98*, 7665–7673.

[37] L. Spanhel, M. Hasse, H. Weller, A. Henglein, *J. Am. Chem. Soc.* **1987**, *109*, 5649–5655.

[38] J. Rockenberger, L. Troger, A. Kornowski, T. Vossmeyer, A. Eychmüller, J. Feldhaus, H. Weller, *J. Phys. Chem. B* **1997**, *101*, 2691–2701.

[39] a) Y.-W. Jun, S.-M. Lee, N.-J. Kang, J. Cheon, *J. Am. Chem. Soc.* **2001**, *123*, 5150–5151; b) O. Dag, S. Alayoglu, C. Tura, O. Celik, *Chem. Mater.* **2003**, *15*, 2711–2717; c) B. A. Simmons, S. Li, V. T. John, G. L. McPherson, A. Bose, W. Zhou, J. He, *Nano Lett.* **2002**, *2*, 263–268.

[40] a) H. Zhao, E. P. Douglas, B. S. Harrison, K. S. Schanze, *Langmuir* **2001**, *17*, 8428–8433; b) L. Qi, H. Colfen, M. Antonietti, *Nano Lett.* **2001**, *1*, 61–65; c) Y. Ma, L. Qi, J. Ma, H. Cheng, W. Shen, *Langmuir* **2003**, *19*, 9079–9085; d) C.-S. Yang, D. D. Awschalom, G. D. Stucky, *Chem. Mater.* **2002**, *14*, 1277–1284.

[41] a) J. Huang, K. Sooklal, C. J. Murphy, H. J. Ploehn, *Chem. Mater.* **1999**, *11*, 3595–3601; b) L. H. Hanus, K. Sooklal, C. J. Murphy, H. J. Ploehn, *Langmuir* **2000**, *16*, 2621–2626; c) B. I. Lemon, R. M. Crooks, *J. Am. Chem. Soc.* **2000**, *122*, 12886–12887.

[42] a) S. P. Moulik, G. C. De, A. K. Panda, B. B. Bhowmilk, A. R. Das, *Langmuir* **1999**, *15*, 8361–8367; b) M. P. Pileni, *J. Phys. Chem.* **1993**, *97*, 6961–6973.

[43] a) T. Hirai, M. Miyamoto, I. Komasawa, *J. Mater. Chem.* **1999**, *9*, 1217–1219; b) S. Y. Lu, M. L. Wu, H. L. Chen, *J. Appl. Phys.* **2003**, *93*, 5789–5793; c) H. Sato, Y. Tsubaki, T. Hirai, I. Komasawa, *Ind. Eng. Chem. Res.* **1997**, *36*, 92–100; d) M. Tata, S. Banerjee, V. T. John, Y. Waguespack, G. L. McPherson, *Colloids Surf., A* **1997**, *127*, 39–46.

[44] X. L. Fang, C. F. Yang, *J. Colloid Interface Sci.* **1999**, *212*, 242–251.

[45] M. Okazaki, L. Washio, Y. Shibasaki, M. Ueda, *J. Am. Chem. Soc.* **2003**, *125*, 8120–8121.

[46] Z. Bo, J. Qiu, J. Li, A. D. Schluter, *Org. Lett.* **2004**, *6*, 667–669.

[47] F. Gröhn, B. J. Bauer, E. J. Amis, *Macromolecules* **2001**, *34*, 6701–6707.

[48] Z. Q. Zhang, G. Y. Xu, F. Wang, S. L. Dong, Y. J. Chen, *J. Colloid Interface Sci.* **2005**, *282*, 1–4.

[49] B. H. Robinson, C. Toprakcioglu, J. C. Dore, P. Chieux, *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 13–28.

[50] A. K. Panda, B. B. Bhowmik, A. R. Das, S. P. Moulok, *Langmuir* **2001**, *17*, 1811–1816.

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