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Spherical, Monodisperse, Functional Bridged Polysilsesquioxane Nanoparticles

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ABSTRACT

A method for the synthesis of functional hybrid nanoparticles of uniform size is reported. 1,1′-bis[3-(trimethoxysilyl)propyl]-4,4′-bipyridinium iodide and *N*,*N*′-bis[(3-trimethoxysilyl)propyl]ethylenediamine bridged polysilsesquioxane spherical, monodisperse nanoparticles are prepared utilizing inverse water-in-oil polymerization methods where nanoparticle size can be influenced by adjusting the interfacial tension and monomer concentration. The former are electrochemically active and can be utilized in display devices. Both are polycationic and can be used as carriers for polyanions such as DNA and construction of layer-by-layer architectures.

The utility of many functional materials including organic polymers, inorganic oxides, and semiconductors is enhanced significantly by the fact that they can be produced as uniform spherical particles. A significant amount of research has taken advantage of micro- and nanoparticle technology in such fields as chromatography,[1] drug and gene delivery,[2−7] bioimaging,[8] catalysis,[9] optical,[10,11] electronic,[12,13] and magnetic[14] applications. Silica-based materials occupy a large portion of such research. Methods, such as the Stöber process,[15,16] have been developed to produce monodisperse spherical silica particles that range in size from millimeters to nanometers. This, coupled with the ability to modify the surface with organics, are key factors that contribute to their utility and importance.

Bridged polysilsesquioxane (BPS) xerogels are hybrid network materials that have organic and inorganic domains dispersed at the molecular level.[17−19] Because the organic group remains an integral component of the material, this variability provides an opportunity to modulate bulk properties such as porosity, thermal stability, refractive index, optical clarity, chemical function, hydrophobicity, and dielectric constant. The organic component not only strongly contributes to the bulk physical properties but also provides function to the material. The fine degree of control over the bulk chemical and physical properties has made these materials candidates for applications in optical devices,[20−23] as high capacity absorbents,[24−26] 3D information storage media,[27] and proton-conducting media for fuel cells.[28,29] BPS are typically prepared in a single step in bulk. The dried xerogels are ground to irregular particles for evaluation. In contrast to silica, with the exception of unique, self-assembling coumarin dimer BPS,[30] there are no methods for producing uniform, spherical BPS nanoparticles.

Here, we describe the first preparation of functional, monodisperse BPS nanospheres. We explore their size dependence on surface tension parameters using inverse water-in-oil emulsion polymerization conditions, where a monomer solution is dispersed in an immiscible medium to afford nanodroplets that undergo sol−gel hydrolysis and condensation. Two bridged silane monomers were utilized to prepare nanoparticles of different compositions to demonstrate the generality of this method. One type of nanoparticle is derived from 1,1′-dipropyl-4,4′-bipyridinium diiodide **1**. These molecules, known as viologens, are electrochromic, exhibiting an intense absorption band in the violet region of the spectrum upon electrochemical reduction.[31] Viologen-containing materials find commercial applications in autodimming mirrors[32,33] as well as potential applications in electrochromic displays.[34] The second class of sol−gel nanoparticles is prepared from *N*,*N*′-bis[(3-trimethoxysilyl)propyl]ethylenediamine **2**. Bulk sol−gel glasses prepared from this precursor are known to have thermoresponsive properties,[35] selective protein uptake and release properties,[36] and have been found to remove copper and aromatic phenol impurities from aqueous solutions when prepared as copolymers with phenylene-bridged silanes.[37]

Monomer **2**, 1,1′-bis[3-(trimethoxysilyl)propyl]-4,4′-bipyridinium iodide, was prepared from the corresponding 4,4′-bipyridyl **1** and 3-iodopropyltrimethoxysilane (Scheme 1).[38]

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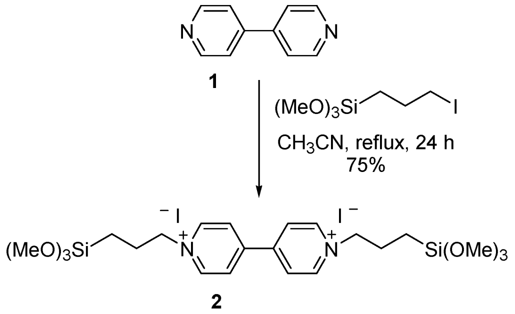
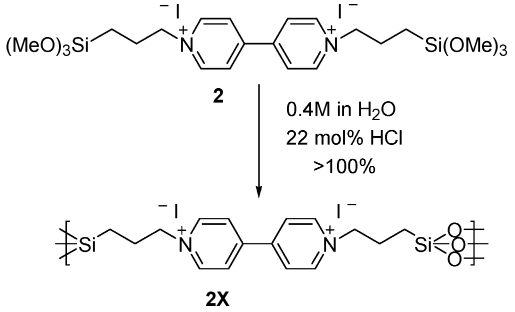
Scheme 1. Synthesis of 1,1′-Bis[3-(trimethoxysilyl)propyl]-4,4′-bipyridinium Iodide **2**



Scheme 2. Synthesis of 1,1′-Bis[3-(trimethoxysilyl)propyl]-4,4′-bipyridinium Iodide Bridged Polysilsesquioxane **2X**



A 0.4 M aqueous solution was determined to reach gelation in 13 min in the presence of HCl, yielding glassy, transparent, orange gels **2X** (Scheme 2).

Sol−gel polymerization in emulsions have been used in the past for the preparation of ORMOSIL nano- and microparticles.[2,4−6,8,11,39−42] We have utilized the emulsion polymerization approach for the first time to yield BPS nanoparticles. These materials are marked by their high loading of functional groups (unattainable for surface modified silica), chemical and thermal stability, and in contrast to ORMOSILs, with a high degree of porosity. The emulsions were prepared using NP-5 as the surfactant and 1-hexanol as the co-surfactant to disperse 0.4 M aqueous monomer solutions in cyclohexane. Several of the formulations resulted in a microemulsion, characterized by its thermodynamic stability and nanometer-sized droplets.[43]

After addition of catalyst (HCl), the emulsions were allowed to age for 48 h (without stirring) to provide time for the formation of stable, solid BPS gel particles. The particles were precipitated with ethanol and washed with water to remove residual surfactant. The conditions are summarized in Table 1. To determine particle size and distribution, wet gel particle microemulsions were analyzed by dynamic light scattering. The samples were also drop-deposited onto Si wafer substrates, allowed to dry over a period of 24 h, then analyzed by scanning electron microscopy.

Table 1: Emulsion Polymerization Conditions of Nanoparticles Prepared from **1**

entry	solvent[a]	surfactant (mL)[b]	co-surfactant (mL)[c]	particle size (nm) [d]
1	cyclohexane	1.6	1.6	40 ± 8
2	cyclohexane	0.8	0.8	218 ± 56
3	cyclohexane	0.55	0.55	270 ± 100
4	cyclohexane	0.4	0.4	220 ± 160
5	cyclohexane	2.5	2.4	irregular

[a] The amount of solvent was kept constant at 7.7 mL. [b] NP-5. [c] *n*-Hexanol. [d] Average diameter of dried xerogel particles.

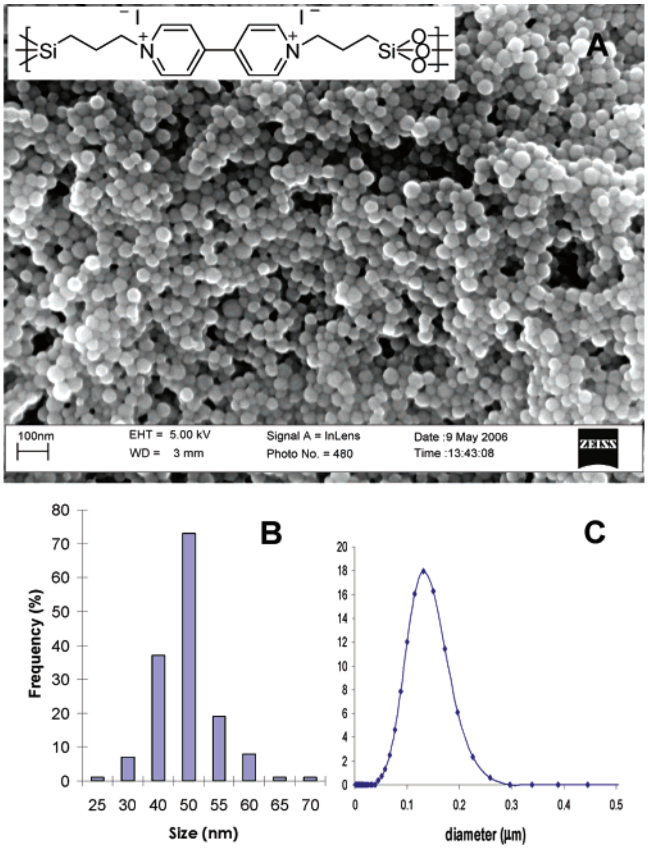
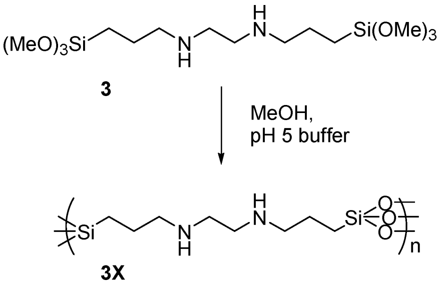


Figure 1. BPS nanoparticles **2X** (entry 1, Table 1). (A) Scanning electron micrograph of dried xerogel (B) Size distribution of the particles in (A). (C) Size distribution of wet gel particles in microemulsion.

While the emulsion stability was the same for all five formulations reported in Table 1, only entries 1 and 2 yield relatively monodisperse spherical particles. The SEM image and its corresponding size distribution (Figure 1a and b, respectively) reveal that particles in entry 1, Table 1, (solvent/surfactant v/v ratio is 2.4:1) are spherical and relatively monodisperse in size with an average diameter of 43 ± 8 nm. The light scattering data of the microemulsion prepared under the same conditions (Figure 1c) shows a monomodal distribution centered around 120 ± 36 nm. The smaller average particle size of the SEM data compared to the wet gel diameters is due to a 95% volume drop upon drying to a xerogel.

The internal structure of the BPS nanoparticles was investigated using transmission electron microscopy (see Supporting Information). The material was found to be uniform and featureless with no apparent phase separation or long-range order.

Scheme 3. Sol−Gel Material **3X** Prepared from *N*,*N*′-Bis[(3-trimethoxysilyl)propyl]ethylenediamine **3**



It was anticipated that the viologen nanoparticles would be electrochemically active. A dispersion of 43 nm particles in 0.1 M $KCl_{(aq)}$ was analyzed by cyclic voltammetry. A reversible reduction wave was observed with a reduction potential of −0.530 V against SCE. This value is within the range of dialkyl-substituted bipyridiniums (1,1′-dipropyl-4,4′-bipyridinium iodide's first reduction potential is −0.680 V vs SCE).[31] Such electrochemical properties and the uniform nanometer size make these materials ideal candidates for incorporation into fast electrochromic devices. Devices incorporating these particles will be reported at a future date.

Ethylenediamine BPS nanoparticles **3X** were prepared from commercially available *N*,*N*′-bis[(3-trimethoxysilyl)propyl]ethylenediamine **3** (Scheme 3). Monomer **3** undergoes near instantaneous gelation under standard sol−gel polymerization conditions, therefore conditions were modified to decrease the reaction rate and permit thorough mixing. At pH 5, sol−gel polymerization of bridged silane monomers is slowest.[44] Thus, in a potassium hydrogen phthalate/NaOH buffer (pH 5.0) and with 0.1 M monomer concentration, gelation occurred after approximately 1 min.

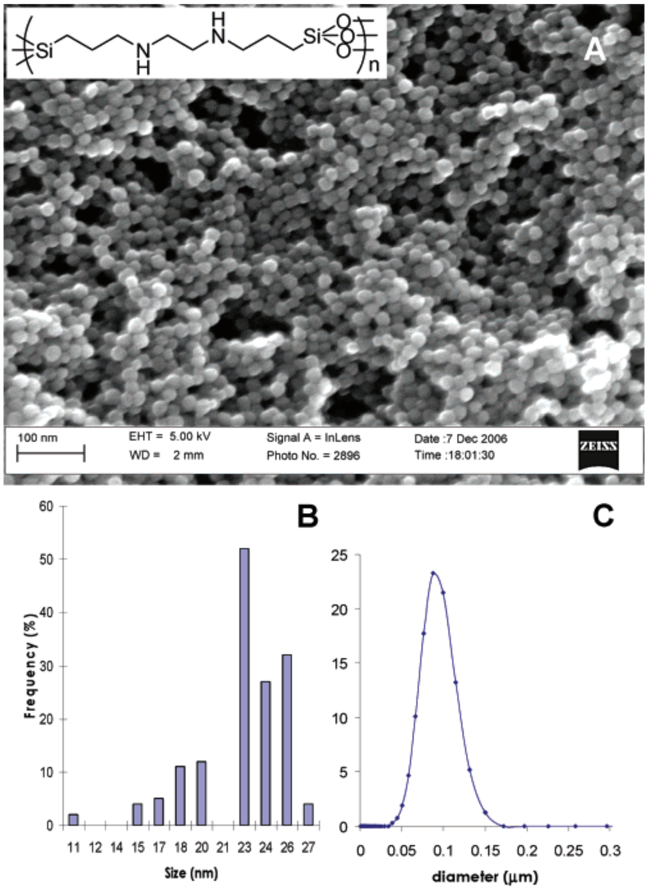


Figure 2. BPS nanoparticles **3X** (entry 2, Table 1). (A) Scanning electron micrograph of dried xerogel. (B) Size distribution of the particles in (A). (C) Size distribution of wet gel particles in microemulsion.

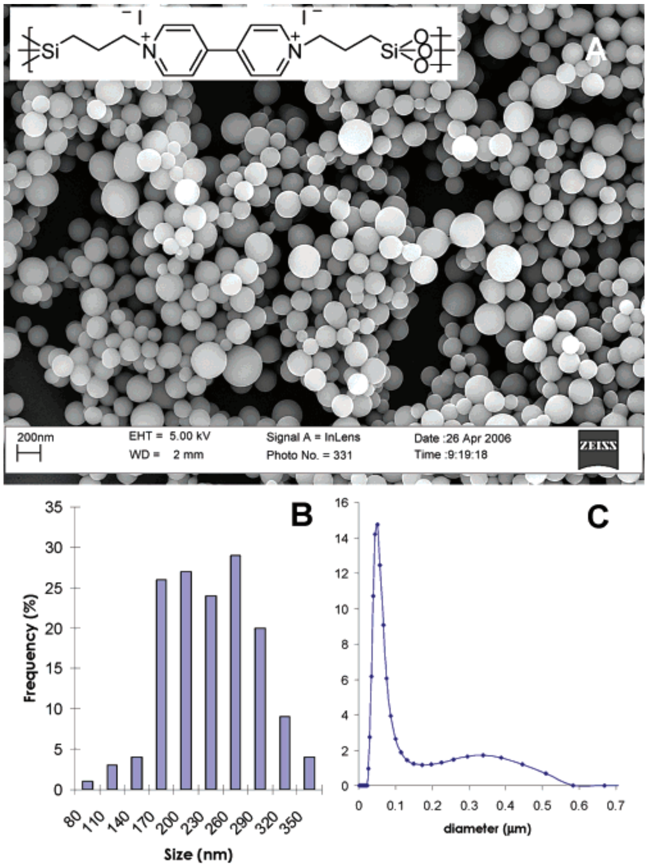


Figure 3. BPS nanoparticles **2X** (entry 2, Table 1). (A). Scanning electron micrograph of dried xerogel. (B) Size distribution of the particles in (A). (C) Size distribution of wet gel particles in microemulsion.

These sol−gel conditions were employed for the microemulsion study. The surfactant conditions were as in entry 2 of Table 1. Interestingly, the average dried xerogel particle diameter of 22 ± 3 nm (Figure 2) is considerably smaller than that of the 1,1′-bis[3-(trimethoxysilyl)propyl]-4,4′-bipyridinium iodide BPS (218 ± 56 nm) prepared under the same emulsion conditions (Figure 3).

This can be attributed to two factors. First, the interfacial tension of the emulsion is decreased due to the presence of a substantial amount of methanol in the sol−gel droplets (the monomer is supplied as 62% solution in methanol), whereas the bipyridinium monomer is dissolved in water and methanol is only present due to hydrolysis of the methoxy groups. In fact, light scattering data of aged (48 h) microemulsions of the **3X** and **2X** samples (polymerization conditions for both are as in Entry 2, Table 1) show a significant difference in droplet size (Figures 2c and 3c, respectively). The **2X** data reveal a bimodal size distribution. While the calculated median particle size is 51 ± 84 nm, a substantial amount of the particles is in the 300 nm range. The median diameter of **3X** particles is much lower (83 ± 19 nm). This would be expected from the decrease in the interfacial tension. The second major contribution to the decrease in particle size is the 4-fold decrease of monomer concentration. This results in a more substantial volume drop of the dried xerogels. Importantly, both the concentration variable and adjustments in interfacial tension can be used to fine-tune particle size.

In conclusion, an inverse oil/water emulsion has been developed for the first synthesis of bridged polysilsesquioxane spherical nanoparticles. We have shown that their size can be influenced by changes in interfacial tension of the emulsions as well as monomer concentration. This approach is being extended to synthesize nanoparticles that incorporate a broad range of organic bridging groups as well as preparation of spheres in the micrometer range for chromatographic applications. The BPS nanoparticles described in this report incorporate electrochromic and pH responsive organic functional groups. In contrast to surface-modified ORMOSIL nanoparticles, these materials exhibit large functional group loadings distributed uniformly throughout the material.[5] In addition, both the bipyridinium and *N*,*N*′-bis[(3-trimethoxysilyl)propyl]ethylenediamine containing nanoparticles are polycationic, rendering them ideal carriers for polyanions such as DNA and for the assembly of core−shell architectures via the layer-by-layer technique. The electrochemical responsiveness of bipyridinium can also be utilized to trigger the release of adsorbed anions.[45]

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Supporting Information Available: Experimental details; TEM images of 1,1′-bis[3-(trimethoxysilyl)propyl]-4,4′-Bipyridinium iodide BPS **2X** particles. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Unger, K. K.; Kumar, D.; Grun, M.; Buchel, G.; Ludtke, S.; Adam, T.; Schumacher, K.; Renker, S. *J. Chromatogr., A* **2000**, *892*, 47−55.

(2) Barbe, C. B., John; Kong, L.; Finnie, K.; Lin, H. Q.; Larkin, M.; Calleja, S.; Bush, A.; Calleja, G. *Adv. Mater* **2004**, *16*, 1959−1966.

(3) Singh, M.; Briones, M.; Ott, G.; O'Hagan, D. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 811−816.

(4) Roy, I.; Ohulchanskyy, T. Y.; Bharali, D. J.; Pudavar, H. E.; Mistretta, R. A.; Kaur, N.; Prasad, P. N. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 279−284.

(5) Bharali, D. J.; Klejbor, I.; Stachowiak, E. K.; Dutta, P.; Roy, I.; Kaur, N.; Bergey, E. J.; Prasad, P. N.; Stachowiak, M. K. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 11539−11544.

(6) Roy, I.; Ohulchanskyy, T. Y.; Pudavar, H. E.; Bergey, E. J.; Oseroff, A. R.; Morgan, J.; Dougherty, T. J.; Prasad, P. N. *J. Am. Chem. Soc.* **2003**, *125*, 7860−7865.

(7) Wang, C.; Ge, Q.; Ting, D.; Nguyen, D.; Shen, H. R.; Chen, J. Z.; Eisen, H. N.; Heller, J.; Langer, R.; Putnam, D. *Nat. Mater.* **2004**, *3*, 190−196.

(8) Santra, S.; Bagwe, R. P.; Dutta, D.; Stanley, J. T.; Walter, G. A.; Tan, W.; Moudgil, B. M.; Mericle, R. A. *Adv. Mater.* **2005**, *17*, 2165−2169.

(9) Beydoun, D.; Amal, R.; Low, G.; McEvoy, S. *J. Nanoparticle Res.* **1999**, *1*, 439−458.

(10) Zhu, M. Q.; Zhu, L. Y.; Han, J. J.; Wu, W. W.; Hurst, J. K.; Li, A. D. Q. *J. Am. Chem. Soc.* **2006**, *128*, 4303−4309.

(11) Ow, H.; Larson, D. R.; Srivastava, M.; Baird, B. A.; Webb, W. W.; Wiesner, U. *Nano Lett.* **2005**, *5*, 113−117.

(12) Kaltenpoth, G.; Himmelhaus, M.; Slansky, L.; Caruso, F.; Grunze, M. *Adv. Mater.* **2003**, *15*, 1113−1118.

(13) Jang, J.; Nam, Y.; Yoon, H. *Adv. Mater* **2005**, *17*, 1382−1386.

(14) Yi, D. K.; Lee, S. S.; Papaefthymiou, G. C.; Ying, J. Y. *Chem. Mater.* **2006**, *18*, 614−619.

(15) Stober, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62−69.

(16) Nozawa, K.; Gailhanou, H.; Raison, L.; Panizza, P.; Ushiki, H.; Sellier, E.; Delville, J. P.; Delville, M. H. *Langmuir* **2005**, *21*, 1516−1523.

(17) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306−3319.

(18) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700−6710.

(19) Shea, K. J.; Loy, D. A. *Polym. Mater. Sci. Eng.* **1990**, *63*, 281−285.

(20) Shea, K. J.; Moreau, J. Loy, D. A.; Corriu, R. J. P.; Bour, B. *Functional Hybrid Materials*; Wiley-Interscience: New York, 2004; pp 50−85.

(21) Choi, K. M.; Shea, K. J. *Photonic Polymer Synthesis*; Marcel Dekker: New York, 1998; pp 437−480.

(22) Innocenzi, P.; Lebeau, B. *J. Mater. Chem.* **2005**, *15*, 3821−3831.

(23) Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. *Science* **1999**, *286*, 945−947.

(24) Shea, K. J.; Hobson, S. T.; Tran, J. Hybrid Organic/Inorganic Absorbents. U.S. Patent W0030355452, 2003.

(25) Liu, J.; Feng, X. D.; Fryxell, G. E.; Wang, L. Q.; Kim, A. Y.; Gong, M. L. *Adv. Mater.* **1998**, *10*, 161−165.

(26) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500−503.

(27) Huang, G. T. *Technol. Rev.* **2005**, *108*, 64−67.

(28) Khiterer, M.; Loy, D. A.; Cornelius, C. J.; Fujimoto, C. H.; Small, J. H.; McIntire, T. M.; Shea, K. J. *Chem. Mater.* **2006**, *18*, 3665−3673.

(29) Honma, I.; Takeda, Y.; Bae, J. M. *Solid State Ionics* **1999**, *120*, 255−264.

(30) Zhao, L. H.; Loy, D. A.; Shea, K. J. *J. Am. Chem. Soc.* **2006**, *128*, 14250−14251.

(31) Monk, P. M. S. *The Viologens. Physicochemical Properties, Synthesis and Applications of the Salts of 4,4′-Bipyridine*; John Wiley & Sons: New York, 1998.

(32) Tonar, W. L. B.; Harlan, J.; Siegrist, Kathy E.; Anderson, John S.; Ash, Kevin L. Electrochromic layers and devices comprising same. U.S. Patent 5,679,283, 1999.

(33) Varaprasad, D. V.; Zhao, M.; Dornan, C. A.; Agrawal, A.; Allemand, P.-M.; Lynam, N. R. Electrochromic polymeric solid films, manufacturing electrochromic devices using such solid films, and processes for making such solid films and devices. U.S. Patent 5,910,854, 1998.

(34) Moller, M. T.; Asaftei, S.; Corr, D.; Ryan, M.; Walder, L. *Adv. Mater.* **2004**, *16*, 1558−1562.

(35) Rao, M. S.; Dave, B. C. *Adv. Mater.* **2001**, *13*, 274−276.

(36) Rao, M. S.; Dave, B. C. *J. Am. Chem. Soc.* **1998**, *120*, 13270−13271.

(37) Jayasundera, S.; Burleigh, M. C.; Zeinali, M.; Spector, M. S.; Miller, J. B.; Yan, W. F.; Dai, S.; Markowitz, M. A. *J. Phys. Chem. B* **2005**, *109*, 9198−9201.

(38) Alvaro, M.; Ferrer, B.; Fornes, V.; Garcia, H. *ChemPhysChem* **2003**, *4*, 612−617.

(39) Miller, C. R.; Vogel, R.; Surawski, P. P. T.; Jack, K. S.; Corrie, S. R.; Trau, M. *Langmuir* **2005**, *21*, 9733−9740.

(40) Zoldesi, C. I.; Imhof, A. *Adv. Mater.* **2005**, *17*, 924−928.

(41) Darbandi, M.; Thomann, R.; Nann, T. *Chem. Mater.* **2005**, *17*, 5720−5725.

(42) Hwang, Y. J.; Oh, C.; Oh, S. G. *J. Controlled Release* **2005**, *106*, 339−349.

(43) Strey, R. *Colloid. Polym. Sci.* **1994**, *272*, 1005−1019.

(44) Loy, D. A.; Mather, B.; Straumanis, A. R.; Baugher, C.; Schneider, D. A.; Sanchez, A.; Shea, K. J. *Chem. Mater.* **2004**, *16*, 2041−2043.

(45) George, P. M.; LaVan, D. A.; Burdick, J. A.; Chen, C. Y.; Liang, E.; Langer, R. *Adv. Mater.* **2006**, *18*, 577−581.

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