LA-UR-14-24096

Approved for public release; distribution is unlimited.

Title: Synthesis of Nanoscale Hollow Styrene and Methacrylate Spheres

Author(s): Barker, Madeline T.

Intended for: Report

Issued: 2014-06-06

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Synthesis of Nanoscale Hollow Styrene and Methacrylate Spheres

Madeline Barker
mtbarker@lanl.gov
9 June 2014

1. Introduction

Hollow polymer nanocapsules are ideal candidates for pore forming microballoons in syntactic foams. With diameters ranging from nanometers to microns, the spheres have been studied for use in drug delivery, nanoreactors, or nanosensors. Using polymer spheres rather than glass beads seen commercially would enable the synthesis of ultra-low density syntactic foams. Our group has postulated that hollow polymer nanocapsules with a diameter ranging 100 – 200 nm would give ideal ultra-low density foams.

Polymerizing hollow spheres within a vesicle bilayer is a growing field.¹⁻¹¹ The inside of a bilayer is hydrophobic and can house monomers and cross-linkers that can be polymerized, primarily by UV radiation in the presence of a photoinitiator. Biological phospholipids readily form vesicles; however, they pose a disadvantage in many polymeric studies because of their sensitivity to a variety of environmental factors.^{2,4,10} Charged single-tail surfactants also form vesicles sensitive to concentration and temperature. The self-assembly of vesicles has been widely studied for decades.¹³⁻²¹ Catanionic mixtures refer to vesicles formed from cationic and anionic surfactants in aqueous solutions. Marques *et al.* define catanionic mixtures as “pseudoternary aqueous mixtures of two oppositely charged surfactants which display interesting interfacial and phase behavior properties, determined by surfactant mixing ratio, total concentration, and molecular structure.”¹⁵ The stability of the catanionic vesicles in water is not fully understood, but Kaler *et al.* show that the catanionic mixtures acting as a zwitterionic surfactant are more stable than “conventional vesicles prepared by mechanical disruption of insoluble liquid crystalline dispersions.”²¹ Chiruvolu *et al.* concluded that the presence of excess cationic surfactant creates electrostatic forces between the two layers, which are responsible for the repulsion fortifying the bilayer and the reason why aggregates do not form.¹⁷

Single-tailed surfactants do not always self-assemble into vesicles. Other structures include micelles, micellar rods, disks, perforated disks, and flexible or planar bilayers. In their review, “Spontaneous Formation of Vesicles,” Šegota and Težak said, “Because of their chemical structure, surface-active substances, amphiphiles, show their ability of self-organization in the solvents, forming self-assemblies with a large variety of morphologically different

Packing parameter	Shape of the cross-section	Expected structure of associates
$< 1/3$	cone	spherical micelle
$1/3 - 1/2$	truncated cone	rodlike micelle
$1/2 - 1$	truncated cone	flexible bilayer, vesicle
≈ 1	cylinder	planar bilayer

Figure 1: Šegota and Težak's¹² structure of surfactants based on geometrical and packing parameters, modified from Hiemenz²²

structures.”¹² They partly attribute the structural behavior to the geometrical parameters and packing parameter ranges of the surfactants shown in Figure 1. The packing parameter, p , is defined as the volume of the hydrocarbon tail of the surfactant, v , divided by the product of the area of the hydrophilic head group area, a , and the optimal chain length of the tail, l , ca. 80% of the fully extended chain when in solution.^{12,14}

$$p = \frac{v}{al}$$

A higher packing parameter for truncated cones, $p = \frac{1}{2} - 1$, gives a flexible bilayer where a lower packing parameter for truncated cones, $p = \frac{1}{3} - \frac{1}{2}$, gives a micellar rod. The final two packing parameters, $p < \frac{1}{3}$ and $p=1$, form spherical micelles and planar bilayers, respectively. To form a vesicle, a truncated cone with high packing parameter is required. The hydrophilic heads of the cationic and anionic surfactants electrostatically interact while the hydrophobic tails of a surfactant taper together to form the hydrophobic bilayer interior. The catanionic mixtures have a higher packing parameter than the individual surfactants due to the “charge neutralization by ion-pairing coupled with the release of hydration water and screening.”¹³ Surfactants’ structures are also affected by external factors and can change if external forces alter the thermodynamic stability.^{12,19}

The Pinkhassik group provides the base method for this study. Although they have looked at concurrent loading of monomers, cross-linking agents, and surfactants alongside diffusion loading of monomers and cross-linking agents into prepared surfactant vesicles, this study solely performs concurrent loading like that seen in Figure 2. Our group adapted the procedure from Kim *et al.*. Concurrent loading was chosen because it is a one-pot preparation step and the hollow polymer nanocapsules that form from diffusion loading with high surfactant concentration are more susceptible to collapse when dried and imaged by transmission electron microscopy.¹

Figure 2: Kim *et al.*'s scheme showing concurrent loading of monomer with surfactant followed by UV photopolymerization to give ca. 200 nm diameter hollow polymer nanocapsules¹

2. Experimental

2.1. Chemicals

Divinylbenzene (DVB), *tert*-butyl styrene (tBS), 4-methyl styrene (4MeS), styrene (Sty), butyl methacrylate (BMA), *tert*-butyl methacrylate (tBMA), and ethylene glycol dimethacrylate (EGDMA) were bought from Sigma-Aldrich and passed through a small plug of inhibitor remover and cotton. The term “monomers” as used in this paper includes all monomers and cross-linking agents. Photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was obtained from Sigma-Aldrich and Irgacure 819 (I819) was obtained from Ciba Specialty Chemicals; both were used without further purification. The surfactants, cetrimonium *p*-tosylate (CTAT), cetrimonium bromide (CTAB), sodium dodecylbenzenesulfonate (SDBS), and sodium dodecyl sulfate (SDS)

were purchased from Sigma Aldrich and used as received. ACS certified methanol (MeOH) was purchased from Fisher Scientific. Deionized water ($>1\text{ M}\Omega\cdot\text{cm}$; Millipore, USA) was used in all experiments.

2.2. Methods

Concurrent Loading. Set concentrations of all reagents in 3 mL DI water were determined based on the procedure described by Kim *et al.*. Surfactant amounts were held constant at CTAT (63.5 mg, 0.140 mmol), SDBS (4.5 mg, 0.013 mmol), CTAB (63.5 mg, 0.174 mmol), and SDS (4.5 mg, 0.016 mmol) for both combinations and regardless of monomer type. Monomers were loaded in a 3:1 molar ratio of total monomer (sum of monomers) to total surfactant (sum of cationic and anionic surfactants). Photoinitiators were loaded at 0.05% of the total surfactant molar amount. Sample preparation was carried out in 20 mL scintillation vials. Solutions were stirred and heated for 30 min at ca. 40 °C. A 0.2 μm Whatman Nylon, 0.2 μm Whatman PTFE with GMF, or 0.2 μm Whatman Nylon with GMF syringe filter was used to extrude the samples ten times. Samples were transferred into quartz cuvettes (Q) with 10.0 mm path lengths and 3.5 mL volumes fitted for screw caps. It should be noted that sample names correspond to notebook sample labelling.

Photopolymerization of Hollow Sphere Nanocapsules. The headspace of the cuvettes was purged with nitrogen gas for 5 min. An incubation chamber made out of aluminum foil was used for UV irradiation of the samples by a short/long wave UV lamp. The samples with DMPA were irradiated with UV light of $\lambda = 254\text{ nm}$ for 2 hours while the samples with I819 were irradiated with UV light of $\lambda = 365\text{ nm}$ for 2 hours. The nanocapsules were precipitated with 0.2 μL 3M NaCl in 20 mL MeOH in a Thermo Scientific CL2 benchtop centrifuge. Washes of varying volume and compositions followed: 5 mL MeOH/5 mL DI water, 20 mL MeOH, three consecutive washes of 10 mL MeOH/10 mL DI water, 5 mL MeOH/5 mL DI water, 10 mL MeOH, and 5 mL MeOH. Centrifugation was done for 10 min set at 5000 RPM while the working RMP was ca. 3600 RPM. Samples were stored in ca. 2 mL methanol.

2.3. Spectroscopy

UV-Vis Spectroscopy. UV-Vis experiments were performed on a Varian Cary 5000 UV-Vis-NIR Spectrophotometer using a quartz cuvette (QS) of 10.0 mm optical path length, and DI water as a standard. One drop of sample was added to 3.5 mL of DI water in the cuvette prior to measurements.

Dynamic Light Scattering. (DLS) Hydrodynamic diameter measurements were collected using a Beckman Coulter Delsa™ Nano C Particle Analyzer. Samples were measured at 25 °C at a fixed scattering angle of 165° using a dual 30 mW laser diode that operates at 658 nm. Samples were measured in the reaction quartz cuvettes without dilution. Each data point was an average of 70 scans. Data was analyzed using the CONTIN size analysis method. Graphs were prepared following a Brookhaven Instruments Corporation White Paper by Weiner.²³

2.4. Scanning Electron Microscopy (SEM)

Micrographs were obtained with an FEI Inspect F SEM (Materials Science Laboratory). To prepare the sample for analysis, an SEM pin stub specimen mount was

covered with double sided adhesive conductive carbon tape. A drop of sample was placed on the tape, and solvent was allowed to evaporate before the sample and pin were dried under vacuum for 10 min. The samples were then coated with palladium/gold using an EEFA® Carbon Coater and Sputter Coater.

3. Results and Discussion

3.1. Concurrent Loading and Photopolymerization

Before UV exposure, all solutions are cloudy due to some insolubility of the monomers in water. When I819 is used as an initiator, the solutions have a slightly yellow tint where solutions with DMPA are white. In either case, the solutions are translucent and colorless after photopolymerization. Some solutions were left on the benchtop overnight before precipitation and washings while others were worked up the same day. Solutions left for ca. 15 hours thickened overnight to a honey-like consistency. When precipitated and washed, nanocapsules are white and opaque.

Kim *et al.* used an extruder, but at this point in research, only syringe filters were available. The three syringe filters used, 0.2 μm Whatman Nylon, 0.2 μm Whatman PTFE with GMF (glass microfiber), or 0.2 μm Whatman Nylon with GMF, were readily available and of the desired pore size. There was no visual change when using the Nylon filter, but both filters with GMF showed a decreased opacity and resulted in the loss of volume within the filter. DI water was pushed through the syringe filter, in attempts to extract reactants, and added to the quartz cuvette to return the reaction volume to 3 mL.

3.2. Spectroscopy

UV-Vis Spectroscopy. For measurements, cuvettes were filled with 3.5 mL DI water to which a drop of sample was added. UV-Vis spectroscopy was performed based on the results of Dergunov *et al.*,⁹ which showed the disappearance and emergence of peaks over the course of polymerization. Our results did not show peak shifts but did show a decrease in absorbance after UV exposure for styrene-based experiments, as shown in Figure 4.

Figure 3: UV-Vis Absorption spectra of styrene-based photoreactions showing a decrease in absorption before and after polymerization (left) and methacrylate-based photoreactions with no feature to track (right).

Samples 17.099 and 22.099 are tBS cross-linked with DVB. The characteristic peak at 250 nm shows the $\pi \rightarrow \pi^*$ transition of the conjugated system.⁹ Its absorbance

decreases as polymerization occurs because of participation of the vinyl group in polymerization. Although the vinyl peak did not fully disappear, polymerization was ceased after 2 hours. Kim *et al.* irradiated samples for 1.5 hours in a photochemical reactor with 10 lamps.¹ Because only one lamp was used here, extra time was added totaling 2 hours. Samples 19.099 and 20.099 are tBMA/BMA cross-linked with EGDMA. The methacrylate monomers are not as conjugated as the styrene monomers and do not show a characteristic absorbance in the UV-visible spectrum.

DLS. All DLS experiments were performed in the reaction cuvette without dilution. The measurements were taken post UV photopolymerization before surfactant removal. The cumulative undersize distribution graphs (top) presented is weighted by volume and was differentiated to give the differential size distribution graphs (bottom).

Figure 4: Cumulative Undersize (top in black) and Differential Size Distribution (bottom in blue) graphs for DLS hydrodynamic radius experiments of a styrene-based sample (left) and a methacrylate sample (right). Cumulative undersize distribution graphs of narrow distributions should be sigmoidal shaped starting at the origin and ending at a height of 100%. Differential size distribution graphs of narrow distributions should be Gaussian shaped with short tails

Figure 4 shows the cumulative undersize and differential size distribution graphs for tBMA and BMA nanocapsules cross-linked with EGDMA polymerized within CTAT/SDBS vesicles (Sample 19.099) and for Sty nanocapsules cross-linked with DVB polymerized within CTAB/SDS vesicles (Sample 26.130). The cumulative undersize distribution graphs of narrow distributions should be sigmoidal shaped beginning at the origin. The differential size distribution graphs of a narrow distribution should be Gaussian shaped and centered on the modal diameter (diameter at the center of the peak) with short tails. Regardless of polymer type or surfactant pair, these distributions of particle diameter cover a wide range. Sample 19.099 has a Gaussian shape, but there are numerous methacrylate-based nanocapsules with a diameter less than 1 micron and some with a diameter as large as 20 micron. This large distribution of particle size prevents the DLS data from providing a definitive diameter for the sample. Although 95% of sample 26.130 is less than 20 nm as shown in the continuous undersize distribution, 5% of the sample has particles with diameters between 20 and 370 nm causing the long right tail in the differential size distribution graph. The DLS data shows the failure of syringe filters to regulate the diameter of the vesicles used to template the hollow polymer nanocapsules.

3.3. SEM

SEM images of samples show polymeric spheres with diameters ranging from nanometers to microns. These diameters are larger than those determined by DLS which is possibly due to the fact that DLS measures the hydrodynamic radius. There is also the possibility that spheres with diameters in the tens of nanometers were present in the samples imaged and not seen due to SEM resolution, or that the spheres in solution were not present in the drop imaged.

Figure 5: SEM micrographs of nanocapsules after surfactant removal and washings. Sample 18.099 is tBS cross-linked with DVB in CTAB/SDS mixture with I819 (A, B), sample 23.099 is tBMA and BMA cross-linked with EGDMA in CTAT/SDBS mixture with DMPA (C), sample 27.130 is 4MeS cross-linked with DVB in CTAT/SDBS mixture with I819 (D, E), and sample 26.130 is Sty cross-linked with DVB in CTAB/SDS mixture with I819 (F).

Samples 18.099, 27.130, and 26.130 (micrographs A, B, D, E, F) are styrene-based samples, and only sample 23.099 (micrograph C) is a methacrylate-based sphere. Sample 18.099 (A, B) has capsules of different diameters composed of tBS cross-linked with DVB and similar, smooth morphologies. Sample 27.130 (D, E) shows hundreds of nanometer diameter 4MeS cross-linked with DVB nanocapsules. Sample 26.130 (F), Sty cross-linked with DVB, had capsules with a different morphology than any other samples observed. Sample 23.099 (C) is the only methacrylate-based sample pictured because no other methacrylate samples had isolated capsules. The surfactant pairs do not appear to have an effect on size or shape of the capsule. Both pairs, CTAB/SDS and CTAT/SDBS, are used with each monomer and photoinitiator pair, but the cationic and anionic surfactants are not switched allowing each pair to have one benzene ring within the catanionic mixture.

4. Conclusion

Polymer nanocapsules with diameters ranging from hundreds of nanometers to tens of microns were successfully synthesized within a vesicle bilayer by UV

photopolymerization. Diameter ranges were determined by SEM imaging and DLS. The difference in the two is partly due to the nature of DLS, which measures the hydrodynamic radius, and is also a result of the limitations of the SEM instrument used. DLS experiments show wide ranges of hydrodynamic diameter for both styrene- and methacrylate-based samples. UV-Vis spectroscopy was used to monitor the disappearance of the vinyl group in the styrene based experiments in the low UV. The methacrylate samples did not have a feature in the UV-Vis range to follow. Samples using I819 as a photoinitiator are yellow-tinted before but colorless after photopolymerization, while samples using DMPA have a slight white coloring before but are also colorless after photopolymerization. The surfactant pairs, CTAB/SDS and CTAT/SDBS, do not have an effect on shape or size of nanocapsule as determined by the data here.

5. Future Work

The procedure, adapted from Kim *et al.*, will be enhanced with an Avanti extruder using 1000 μ L syringes and 0.2 μ m polycarbonate membranes. This apparatus should ensure hollow polymer nanocapsules with 200 nm diameters. In addition to the incorporation of an extruder, the work up will be improved based on an experiment by Morgan *et al.* that uses acetone instead of a salt solution.¹¹ This change should limit the amount of water used so that 1 L of solvents is not used to wash a 3 mL reaction. Data that measures the wall size of the capsules showing that they are hollow, which SEM imaging cannot verify, will be obtained. Finally, the capsules will be incorporated into a matrix to form ultra-low density syntactic foam.

6. References

- (1) Kim, M. D.; Dergunov, S. A.; Richter, A. G.; Durbin, J.; Shmakov, S. N.; Jia, Y.; Kenbeilova, S.; Orazbekuly, Y.; Kengpeil, A.; Lindner, E.; Pingali, S. V.; Urban, V. S.; Weigand, S.; Pinkhassik, E. *Langmuir* **2014**.
- (2) Pereira da Silva Gomes, J. F.; Sonnen, A. F.-P.; Kronenberger, A.; Fritz, J.; Álvaro Neto Coelho, M.; Fournier, D.; Fournier-Nöel, C.; Mauzac, M.; Winterhalter, M. *Langmuir* **2006**, *22*, 7755.
- (3) Chen, D.; Jiang, M. *Acc. Chem. Res.* **2005**, *38*, 494.
- (4) Changez, M.; Kang, N. G.; Lee, C. H.; Lee, J. S. *Small* **2010**, *6*, 63.
- (5) Changez, M.; Kang, N. G.; Lee, J. S. *Small* **2012**, *8*, 1173.
- (6) McKelvey, C. A.; Kaler, E. W.; Zasadzinski, J. A.; Coldren, B.; Jung, H.-T. *Langmuir* **2000**, *16*, 8285.
- (7) Dergunov, S. A.; Richter, A. G.; Kim, M. D.; Pingali, S. V.; Urban, V. S.; Pinkhassik, E. *Chem. Commun.* **2013**, *49*, 11026.
- (8) Dergunov, S. A.; Miksa, B.; Ganus, B.; Lindner, E.; Pinkhassik, E. *Chem. Commun.* **2010**, *46*, 1485.
- (9) Dergunov, S. A.; Kesterson, K.; Li, W.; Wang, Z.; Pinkhassik, E. *Macromolecules* **2010**, *43*, 7785.
- (10) Ruysschaert, T.; Germain, M.; Pereira da Silva Gomes, J. F.; Fournier, D.; Sukhorukov, G. B.; Meier, W.; Winterhalter, M. *IEE Trans. Nanobiosci.* **2004**, *6*, 49.
- (11) Morgan, J. D.; Johnson, C. A.; Kaler, E. W. *Langmuir* **1997**, *13*, 6447.
- (12) Segota, S.; Tezak, D. *Adv. Colloid Interface Sci.* **2006**, *121*, 51.
- (13) Pevzner, S.; Regev, O.; Lind, A.; Lindén, M. *J. Chem. Soc., Chem. Comm.* **2003**, *125*, 652.
- (14) Ninham, B. W.; Evans, D. F. *Faraday Discuss.* **1986**, *81*, 1.
- (15) Marques, E. F.; Regev, o.; Khan, A.; da Graça Miguel, M.; Lindman, B. *J Phys Chem B* **1998**, *102*, 6746.
- (16) Marques, E. F.; Regev, O.; Khan, A.; da Graça Miguel, M.; Lindman, B. *J Phys Chem B* **1999**, *103*, 8353.
- (17) Chiruvolu, S.; Israelachvili, J. N.; Naranjo, E.; Xu, Z.; Zasadzinski, J. A. *Langmuir* **1995**, *11*, 4256.
- (18) Walker, S. A.; Zasadzinski, J. A. *Langmuir* **1997**, *13*, 5076.
- (19) Bergstrom, L. M.; Skoglund, S.; Edwards, K.; Eriksson, J.; Grillo, I. *Langmuir* **2014**.
- (20) Safran, S. A.; Pincus, P.; Andelman, D. *Science* **1990**, *248*, 354.
- (21) Kaler, E. W.; Murthy, A. K.; Rodriguez, B. E.; Zasadzinski, J. A. *Science* **1989**, *245*, 1371.
- (22) Hiemenz, P. C.; Rajagopalan, R. *Principles of colloid and surfaces chemistry*; Marcel Dekker, Inc.: New York, 1997.
- (23) Weiner, B. B. "What is a Continuous Particle Size Distribution?" Published Online: 2011.