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Laboratory Experiment
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Emulsion Polymerization, Size Determination, and Self-Assembly of Monodispersed Poly(methyl methacrylate) Nanospheres for Photonics

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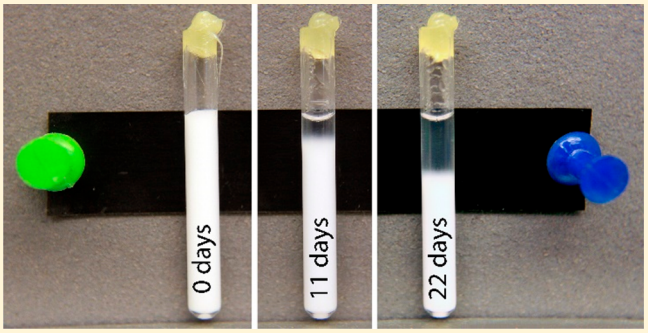
Supporting Information

ABSTRACT: Polymers and nanochemistry are important facets of chemistry. In this experiment, students synthesize monodispersed poly(methyl methacrylate) nanospheres from the addition or chain polymerization of a rapidly stirred aqueous mini-emulsion of methyl methacrylate. The 2,2′-azobis(2-methylpropionamidine) dihydrochloride serves as a heat activated, water-soluble, free radical initiator to polymerize the emulsion droplets starting from their outer edge. The uniform small diameter particles will appear iridescent if they are close-packed and their size is similar to the wavelength of visible light. Students characterize the size of the poly(methyl methacrylate) spheres by four methods: the settling velocity and Stokes' law, evaporative self-assembly of a photonic material and visible spectroscopy, direct measurement using scanning electron microscopy (SEM), and SEM measurement of the silica inverse opal. This experiment increases student collaboration and provides the opportunity to work on multiple experiments at once.



KEYWORDS: *Second-Year Undergraduate, Polymer Chemistry, Analogies/Transfer, Hands-On Learning/Manipulatives, Free Radicals, Nanotechnology, Polymerization, Synthesis*

INTRODUCTION

The 2015 ACS Guidelines from the Committee on Professional Training[1] require that the principles governing macromolecular and nanoscale systems be part of the curriculum for certified graduates. Since this experiment involves an addition or chain polymerization of a mini-emulsion to create monodispersed (uniform-sized) poly(methyl methacrylate) (PMMA) spheres that self-assemble to form photonic nanomaterials, it can serve as a contribution to both of these requirements.

The nonpolar methyl methacrylate starting monomer is immiscible with water, and rapid stirring of a mixture causes small spheres in the form of a mini-emulsion. The water-soluble 2,2′-azobis(2-methylpropionamidine) dihydrochloride eliminates N_2 when heated, and the resulting free radicals serve as the initiator for the polymerization reaction as shown in Scheme 1. If the emulsion globules have a uniform size, then polymerization of the globules produces uniform-sized PMMA spheres.

A few examples of opalescence observed in nature are iridescent beetle shells, peacock feathers, opals, and blue morpho butterflies[2] (Figure 1). Their common feature is a highly regular pattern with a repeat distance similar to the wavelength of visible light. Diffraction occurs when reflected wavelengths of light interact with another reflected wave offset by a regular spacing between units to give destructive wave interference. Some wavelengths of light will not be observed, and this causes the existence of a photonic band gap.[3] Materials that block some wavelengths are useful to manipulate

Scheme 1. Thermal decomposition of water-soluble 2,2′-azobis(2-methylpropionamidine) dihydrochloride (top) generates nitrogen gas and free radicals, which act as initiator (bottom) for polymerization of methyl methacrylate. The chloride counter ion is not shown.

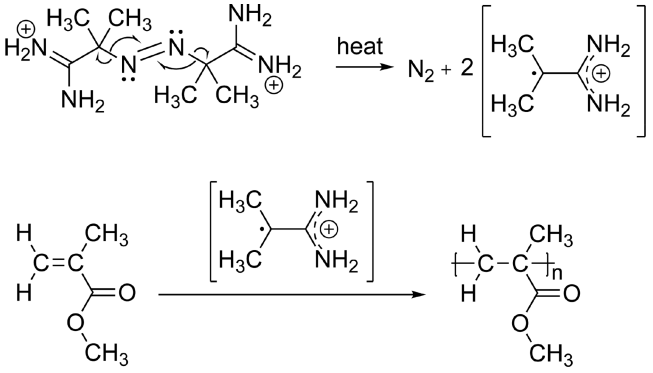


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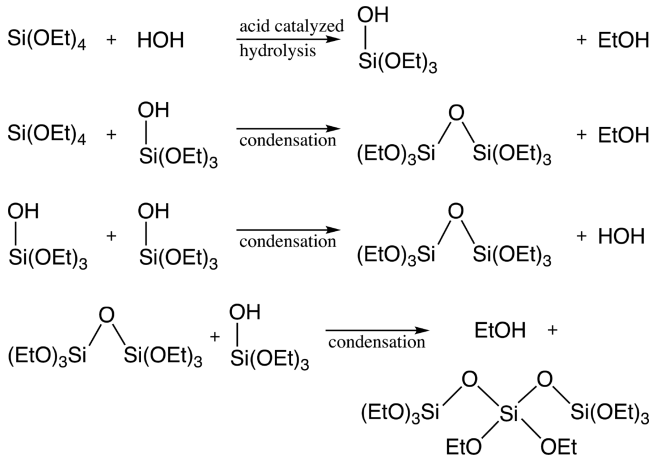
Figure 1. Blue morpho butterfly (*Morpho peleides*) is a natural example of a photonic material. Its color is due to the diffraction of visible light from structural features with a repeat distance similar to the wavelength of visible light instead of color by electronic transition between energy levels.

light in a variety of applications. Photonic crystals are being tested in dye-sensitized solar cells, LEDs, and sensors; moreover, they have promise for optical circuits by trapping photons.[4−6] The wavelength of the photonic band gap depends on the difference in refraction indices in the material, how uniformly the individual units are packed, and the repeat distance.[7] Another goal of this experiment is to provide experience with sources of color that are not due to an electronic transition.

There are two general ways of creating nanomaterials such as photonic materials. The "top-down" approach includes a variety of lithographic methods that use beams of photons, electrons, protons, atoms, or ions to remove material and create a repeating pattern. The "bottom-up" approach uses inertial, capillary, electromagnetic, or intermolecular forces to assemble smaller parts, again to produce a repeating pattern.[8] The produced ∼250 nm PMMA spheres can be close-packed by sedimentation, centrifugation, or evaporative self-assembly to produce a close-packed structure similar to the arrangement of hydrated silica spheres found in opals.[9,10] This structure can serve as a mold for a Stöber condensation polymerization reaction (Scheme 2) and subsequent thermal decomposition of PMMA, resulting in a solid with close-packed holes surrounded by a material with a higher index of refraction and called an inverse opal. Changing the content of the holes allows for investigation of the effect of the index of refraction on the photonic band gap.

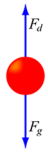
This experiment has students working together to measure the size of the PMMA spheres by multiple methods. A low-cost way of measuring particulate size is to measure their terminal velocity as they fall through a fluid; size is determined by Stokes' law (Box 1) as the nanospheres fall in water. Another technique for measuring particle size is through visible spectroscopy after self-assembly into a photonic material; a modified Bragg's law (Box 2) is used to determine size by visible light diffraction.[11] Third and fourth methods use direct measurement of both the spheres and their inverse opal structure using a scanning electron microscope (SEM). Finally, we have also confirmed these measurements by atomic force microscopy, but we find that technique is slow for class use.

Scheme 2. Stöber condensation polymerization of tetraethylorthosilicate (TEOS) to form Si−O−Si bonds by eliminating water (HOH) or ethanol (EtOH). This reaction repeats to form an amorphous 3-D silica structure.



Box 1. Stokes Law Terminal velocity

Using density and the volume of a sphere, the gravitational force considering buoyancy is $F_g = mg = (\rho_s - \rho_l)\frac{4}{3}\pi(\frac{d}{2})^3 g$, where ρ_s is the density of the solid, ρ_l is the density of the liquid, d is the particle diameter, and g is the gravitational constant. The drag force from Stoke's Law is $F_d = 3\pi\eta v d$, where η is the fluid viscosity and v is the particle velocity. Setting $F_g = F_d$ and rearranging gives the terminal velocity of the particle, $v = \frac{(\rho_s - \rho_l)d^2 g}{18\eta}$. Thus, the rate at which the particles settle is a sensitive measure of their diameter.



Box 2. Modified Bragg Equation

The size of the nanoparticles can be calculated from the wavelength of the absorbance peak (90° incident angle), $\lambda_{peak} = 2d_{sphere}\sqrt{\frac{2}{3}\left\{\left(n_{sphere}\right)^2 f + \left(n_{void}\right)^2\left(1-f\right)\right\}}$, where d_{sphere} is diameter of the close packed spheres and the last term is the effective refractive index where n_{sphere} and n_{void} are the respective indices of refraction for the spheres (1.49 for PMMA) and the void spaces (1.00 for air) and f is the filling fraction for a close packed structure (0.74).

EXPERIMENTAL OVERVIEW

This experiment is a modification and extension of an excellent reported procedure that uses a significantly larger scale.[12,13] This version is scaled 1/1000 for a 25 mL round-bottom flask, which produces more than enough product for student characterization. Similar experiments have been published in this Journal with silica[14,15] and polystyrene.[16,17]

Students create a mini-emulsion by stirring 3.0 mL of methyl methacrylate in 16 mL of water under nitrogen (Supplementary Figure S1). When stirring and temperature are stable, 2,2′-azobis(2-methylpropionamidine) dihydrochloride is added to initiate polymerization (Scheme 1). Factors that affect particle size are temperature and methyl methacrylate concentration.[18] We have observed that variations of 0.5 mL of reactant and 5 °C produce significant differences in sizes.

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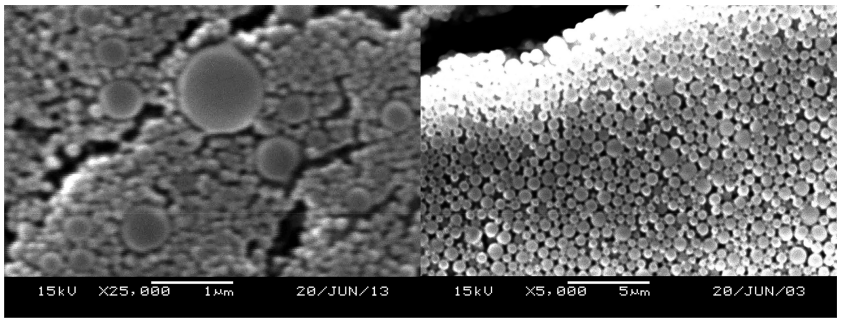

Figure 2. (Left) Large variation in size is seen when the flask is not well-stirred during synthesis. (Right) Without a nitrogen atmosphere to exclude oxygen that could prematurely polymerize the methyl methacrylate, the spheres are not uniform in size.

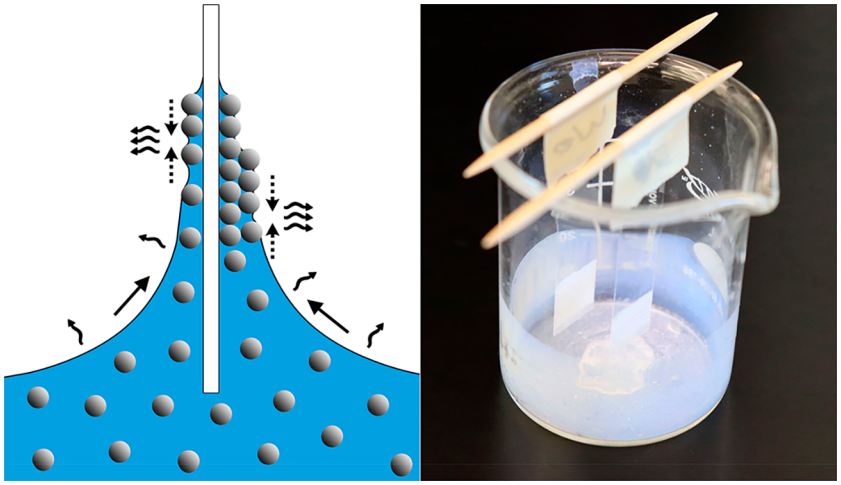

Figure 3. (Left) Scheme showing how self-assembly is performed. Curvy arrows indicate water evaporation that is faster at the upper edge; straight arrows indicate water flow that concentrates the particles and dashed arrows indicate capillary attraction that assembles the particles. (Right) Final result after evaporation of a dilute solution of PMMA nanospheres. The hanging pieces of glass taped to the sticks will fit in the sample compartment of a visible spectrometer to find the absorption maxima (Figure 4). Duplicate samples can be prepared in one 50 mL beaker.

Figure 2 shows the importance of rapid uniform stirring and a nitrogen environment to produce monodispersed spheres. A white suspension occurs in a few minutes. After 40 min of rapid stirring at 70 °C, the round-bottom flask is allowed to cool.

Students then seal culture tubes of the product to prevent evaporation and mount them on a bulletin board to prevent physical disturbances. The samples are aligned with a scale bar and photographs taken every 3 or 4 days to measure the terminal velocity that the spheres reach in water, ∼1 nm/s. The size of the nanospheres is calculated using Stokes' law[19] as shown in Box 1.

Some of the remaining product is diluted 40-fold for evaporative self-assembly onto a glass slide sized to fit in a cuvette chamber. Capillary forces formed by the evaporation on the thin part of the meniscus force the spheres to assemble,[11] as illustrated in Figure 3. Once the solution has slowly evaporated, visible spectroscopy of the slide is recorded (Figure 4) to determine the photonic band gap peak and consequently the size of the spheres as shown in Box 2.

Finally, some product is added to microfuge centrifuge tubes and spun at 2000 rpm for 6 h. Students then remove the supernatant solution and leave the solid in the tube to air-dry over the next few days. Once the product is dry, chunks of self-assembled PMMA spheres are gently transferred into a combustion boat and an acidified ethanol solution of tetraethyl orthosilicate (TEOS) is added. Heating in a tube furnace gives silica glass (Scheme 2), and further heating decomposes the PMMA leaving holes in silica.

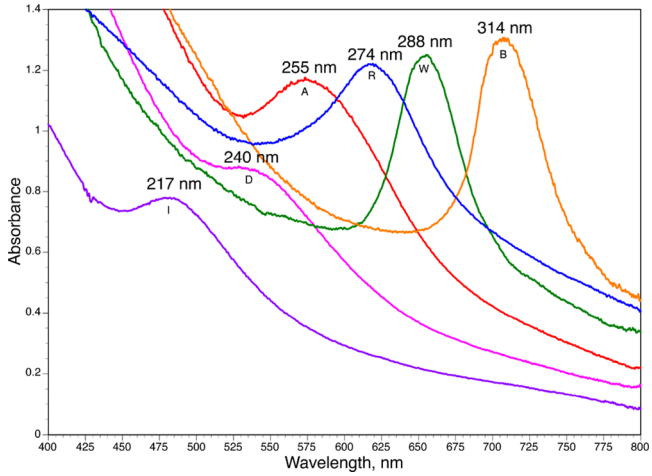

Figure 4. Examples of visible absorbance spectra that show a photonic band gap peak from self-assembled PMMA nanospheres (as prepared in Figure 3). The peaks are labeled with the sphere size calculated according to Box 2. Narrower peaks are due to better close-packing and a narrower distribution of feature spacings. Even moderately assembled samples can still give a peak. The letters match samples in Figures 6 and 7.

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The operator time involves one laboratory period for the initial synthesis and small amounts of additional time to collect data. Ideally, terminal velocity data are obtained by taking a picture every 3−4 days for a month, or at the very least 2 weeks. Groups of three or four students working together are recommended. A suggested schedule is shown in Table 1.

Table 1. Experimental Timeline by Lab Periods

Lab	Activity	Time Period, Min
1	Synthesis. Start Stokes' law experiment. Fill centrifuge tubes. Dilute sample and start self-assembly evaporation.	150−180
Between laboratories: Centrifuge samples several hours. Record Stokes' law data.		
2	Remove excess water from centrifuge tubes. Record Stokes' law data.	15
	Do a different experiment.	?
Between laboratories: Air dry centrifuge tubes. Record Stokes' law data.		
3	Inverse opal into oven. Record Stokes' law data.	15
	Do a different experiment.	?
Between laboratories: Heat inverse opal samples overnight. Record Stokes' law data.		
Midterm break and possibly other lab experiments.		
4	Visible spectroscopy. Record Stokes' law data.	15
	Do a different experiment or take SEM images. SEM may be done by staff.	?
Lab report due.		

HAZARDS

Methyl methacrylate, tetraethyl orthosilicate, and 2,2′-azobis-(2-methylpropionamidine) dihydrochloride are flammable and can cause skin and respiratory irritation. 2,2′-Azobis(2-methylpropionamidine) dihydrochloride is toxic to aquatic life. These materials and leftover solutions should be disposed of as organic waste.

Hydrochloric acid has a high vapor pressure and causes severe skin burns, eye damage, and respiratory corrosion. Inhalation and contact with skin and eyes should be avoided so work should be carried out in a fume hood with protective gloves and goggles.

Syringe needles used for the inert atmosphere during the PMMA synthesis have sharp ends and should be handled with caution. Use appropriate precautions with inert gas supplies.

Blunt needles and syringes should be used for dispensary purposes.

RESULTS AND DISCUSSION

The yield is pretty much 100% or 0%. As the synthesis proceeds, the white color makes success immediately obvious. If the synthesis is successful, large quantities of monodispersed spheres are produced as shown by the same-size spheres for both examples in Figure 5. Multiple methods of measurement all produce similar size results as seen by student results in Figure 6. For further confirmation, opal and inverse opal sizes were measured for one sample by AFM and are shown in Figure S3.

In student hands, the synthesis of the nanospheres works about three out of every four times. The major determining factor is whether the initial stirring produces an emulsion. Stirring too slow leaves a layer of methyl methacrylate floating on the water. Stirring so fast that the stir bar jumps around gives polydispersed spheres. To add reagents, we lift up the condenser and add directly by blunt-needle syringe to the round-bottom flask. This technique noticeably improved our success since it minimized the flask opening time and made sure reactants were added into the flask. This matters most for the initiator, where adding solution is easier than adding a small amount of solid, especially under a nitrogen flow. We and others[18] have found that, even under well-controlled reaction conditions, there is significant variation in product size. Student data where everyone followed the same directions are shown in Figure 6. We do view it as more interesting when each group gets a different size to characterize. Since there is an abundance of product, we have dealt with unsuccessful syntheses by sharing product from another group and that way every group could do the analyses.

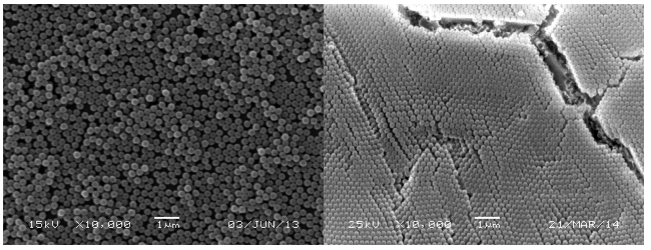

Figure 5. Two different Au/Pd-sputtered PMMA nanosphere samples illustrating typical SEM images from before (left) and after (right) evaporative self-assembly. Close-packing as well as cracking from the drying process can be seen at the right. These observed levels of defects still result in a photonic band gap peak in the visible spectrum. For another example, see Figure S2.

Stokes' law is quite useful in determining size since it gives good results and is low cost, assuming students have a way of taking digital photographs for analysis. An important part of the experimental design is using the black electrical tape supporting the tubes as the scale bar (see abstract image). As shown in Figure 7, each particle batch falls at a constant velocity since the distance/time slope is linear. Figure S4 shows that replicate samples give reproducible results, and the spheres stop falling when they hit bottom. Fluctuations in the data could be from variation in room temperature. If the temperature changes, so does the viscosity of the water[20] (Figure S5), which changes the speed at which the spheres drop. These fluctuations even out over the long period of data collection. The largest error is in setting the initial position of the sample since it is hard to see the meniscus in the white solution. This error also cancels with graphical analysis because determining the slope of the position versus time graph does not depend on the *y*-intercept, which indicates the error in initial sample alignment.

We have observed that spheres above 350 nm in diameter fall too fast to measure at the designated sampling rate. Fast falling also causes them to not self-assemble by evaporative methods.

The quality of evaporative self-assembly of the nanospheres depends on a uniform evaporation rate. If evaporation is uniform, we see clear close packing by the obvious opalescence[21] (Figure S7) and sharp peaks as shown in Figure 4. If the temperature is inconsistent, the sample ends up forming rings that do not always result in a distinct peak in the visible spectrometer. If evaporation did not produce close packing, a lower filling factor results.

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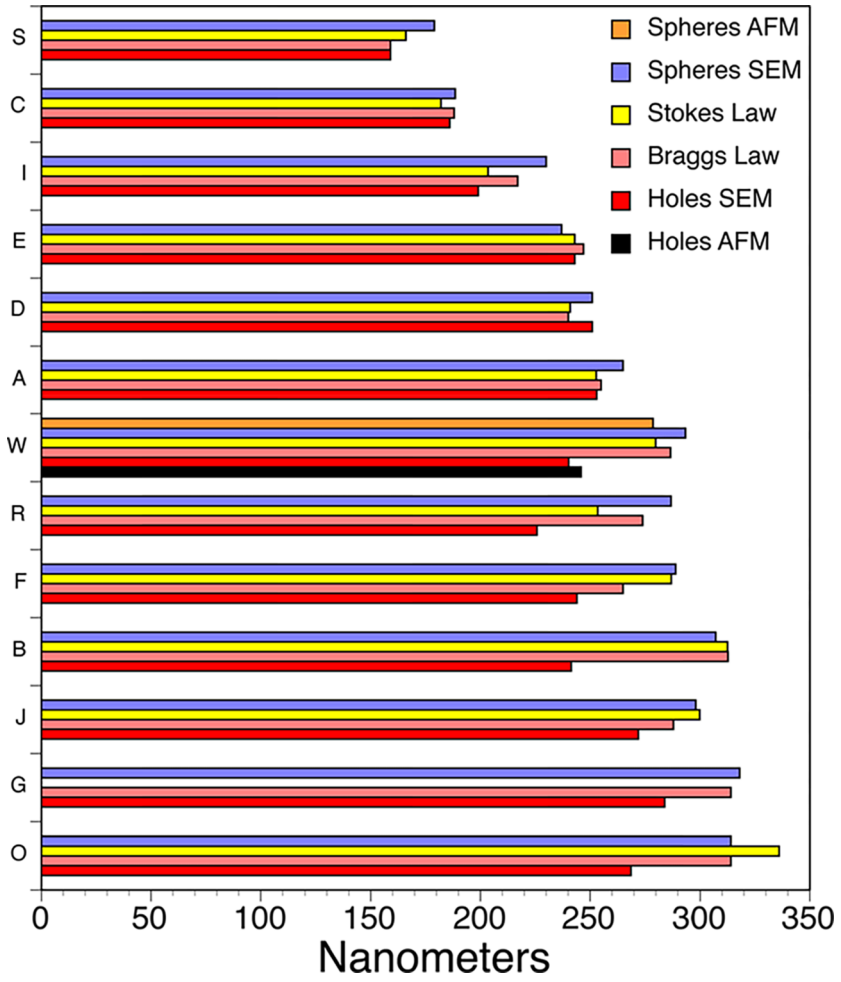

Figure 6. Comparison of method results for 14 different batches of PMMA spheres produced over several years. The sphere size measured by Bragg's law, SEM data of the spheres, terminal velocity from Stokes' law, and SEM data of the silica inverse opal are quite consistent for a given batch but can vary significantly between batches. AFM data were obtained only for sample W; both spheres and holes gave results similar to the other methods. For large nanospheres, the inverse opal size is smaller than the other measurement methods. The letters match the samples in Figures 4 and 7.

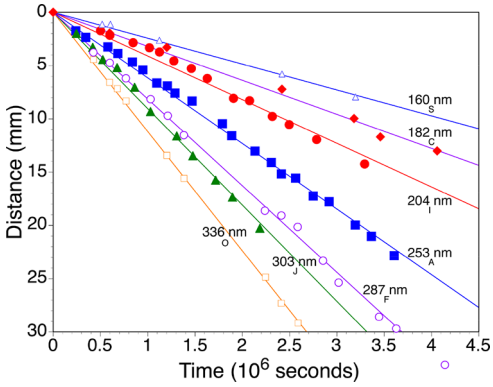

Figure 7. Student results for the Stokes' law terminal velocity measurements based on photographs taken over a few weeks. The lines are labeled with the particle diameter calculated according to Box 1. Two million seconds is about 3 weeks and is enough time to obtain results as the particles drop a cm or two. The letters match samples in Figures 4 and 7.

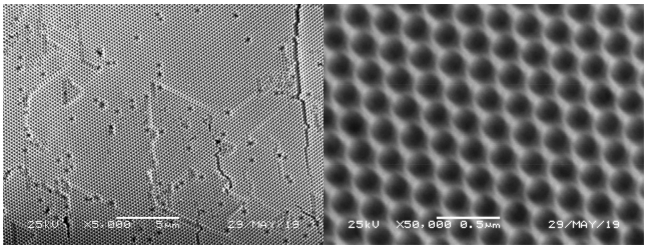

Figure 8. SEM images of the inverse opal prepared using the self-assembled PMMA nanospheres as a template for silica formation and then heating in air to remove the nanospheres. The same sample is shown at different magnifications. (Left) Point defects formed by a missing sphere are noticeable as dark spots. Step edges are seen as light lines. (Right) Close packing of the holes is evident. See also Figures S8 and S9.

SEM data for the inverse opal repeat spacing (Figure 8) are often smaller than all of the other methods of measurement as shown by Figure 6. We have observed that polymerization of TEOS for macroscopic samples results in a smaller replicate than the original mold. The inverse opal does have the ability to show the tunable properties of photonic crystals by adding solvent into the voids;[22] see Figure 9. We use water, ethanol, and toluene for different indices of refraction.

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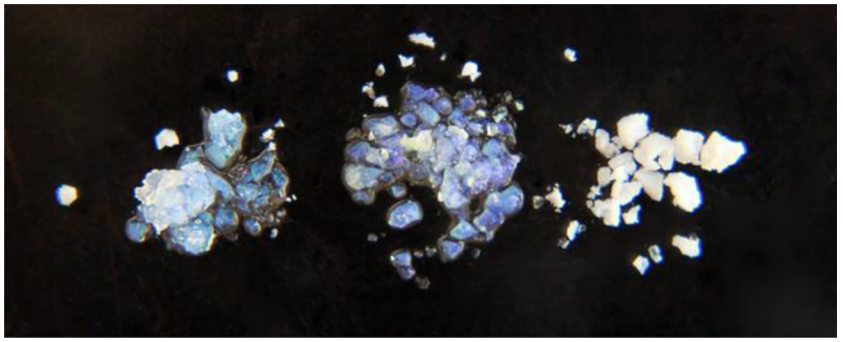

Figure 9. Photograph of the inverse opal with drops of ethanol (left), toluene (center), and without solvent (right). Changing the refractive index of the material in the holes changes the color by changing the wavelength of the photonic band gap.

STUDENT LEARNING

Measuring size in different ways improves confidence in the results and may encourage future practices to confirm results in multiple ways. One of the objectives of these experiments was to allow students to choose which of their methods of size determination was the most accurate. We found that this can be a difficult concept for students to grasp. They tend to prefer the direct SEM measurement of the spheres even though low contrast, curvature, and sample melting are problems. Students practice time management and scheduling to complete this lab in addition to the others being performed at the same time. The extended length illustrates that not all laboratories can be done in one period. This experiment also requires use of physics concepts such as index of refraction and gravitational force connecting class material from other disciplines. Students experienced self-assembly techniques and were able to recognize close packing and defects. This lab also gave an experiential scale to a nanometer, as the terminal velocity of the spheres is about 1 nm/s and it takes a long time to travel at that velocity. Finally, the experiment also gives exposure to photonics and the fundamentals behind photonic crystals as well as exposure to polymer chemistry.

SUMMARY

The PMMA spheres are synthesized through addition or chain polymerization of an alkene, and the inverse material is produced through a condensation polymerization of tetraethylorthosilicate so students gain exposure to two major classes of polymerization. The condensation polymerization is also an example of the Stöber reaction, which is used to produce most oxide nanostructures. This reaction, the evaporative self-assembly, and the observed changes in properties due to size are important from the nanochemistry viewpoint.

In this experiment, students gain exposure to polymers, photonics, and self-assembly to measure the size of the PMMA nanospheres by four different methods. If a SEM is not available or time is limited, the synthesis and the Stokes' law and photonic band gap methods would still provide most of the learning objectives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.9b00621.

Additional supporting figures (PDF, DOCX)
Experimental protocol including student directions and laboratory questions (PDF, DOCX)
Instructor notes and answer key (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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