

Emulsifier-Free Emulsion Polymerization Produces Highly Charged, Monodisperse Particles for Near Infrared Photonic Crystals

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We have developed emulsifier-free, emulsion polymerization recipes for the synthesis of highly charged, monodisperse latex particles of diameters between 500 and 1100 nm. These latexes consist of poly[styrene-(*co*-2-hydroxyethyl methacrylate)] spherical particles whose surfaces are functionalized with sulfate and carboxylic acid groups. These highly charged, monodisperse particles readily self-assemble into robust, three-dimensionally ordered crystalline colloidal array photonic crystals that Bragg diffract light in the near infrared spectral region. By altering the particle number density, the diffraction wavelength can be tuned from ~ 1000 to ~ 4000 nm. © 2002 Elsevier Science (USA)

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INTRODUCTION

Latex polymer colloids are important in many areas of technology, such as in paint and coatings, ceramics processing, and biotechnology (1). These particles are often prepared by emulsion polymerization, which can produce highly monodisperse, spherical particles from polymers such as polystyrene and polymethylmethacrylate.

A group from Dow Chemical Corporation in 1947 was the first to demonstrate the synthesis of monodisperse polystyrene latex colloids (2). This work was followed by development of additional synthetic approaches that produce monodisperse colloidal particles. These approaches include emulsion polymerization, seeded emulsion polymerization, emulsifier-free emulsion polymerization, precipitation polymerization, and dispersion polymerization (3–31). These monodisperse particles can form highly ordered, close packed structures which Bragg diffract light.

Krieger *et al.* (2b, 32) showed in 1968 that monodisperse colloidal particles with covalently attached ionizing groups will self-assemble in solution into highly ordered, non-close-packed three-dimensional arrays, known as crystalline colloidal arrays

(CCAs), where the lattice spacings are much greater than the particle diameters. These charged particles electrostatically repel one another, and the system minimizes its free energy by self-assembling into either a body-centered cubic (BCC) or a face-centered cubic (FCC) lattice (2b, 32–38).

These monodisperse colloidal particle dispersions undergo phase transitions between macroscopic long-range ordered BCC and FCC crystalline phases. In addition, decreases in the particle repulsive interactions (induced, for example, by increasing the solution ionic strength) will cause these CCAs to undergo a phase transition to a liquid-like ordered phase that shows only short-range ordering. At even higher ionic strengths, the CCA undergo phase transitions to an unordered gas-like phase, where the particle positions are uncorrelated (39–41). Since these phase transitions depend mainly upon the electrostatic interactions between the colloidal particles (42, 43), they depend upon the particle charge, screening by other ionic species (44), particle size polydispersity (45), charge polydispersity, and the particle volume fraction (44). It is easy to induce phase transitions by addition of micromolar amounts of salt, thus screening the repulsive interactions. The most robust crystalline phases occur when electrostatic interactions are maximized, i.e., at the highest particle charge densities and at the lowest solution ionic strengths.

Alfrey, Bradford, and Vanderhoff were the first to study the light scattering properties of CCA (2a) and showed that these BCC or FCC crystal lattices efficiently Bragg diffract light (34, 46). This CCA Bragg diffraction results in unique optical phenomena that give these materials applications in optics and spectroscopic instrumentation. We were the first to demonstrate that CCA act as photonic crystals, which function as narrow band radiation filters (34, 47). These CCA have also been immobilized within hydrogel matrices (polymerized CCA or PCCA), and this composite material has been used to make photonic crystals that show nanosecond optical switching (34e–f, 48). These PCCA can be functionalized with molecular recognition agents to create chemical sensing materials that sense specific analytes by undergoing hydrogel volume phase transitions (49). These volume changes cause diffraction wavelength shifts proportional to the analyte concentration (49).

Our interest in fabricating mesoscopically, periodic, smart materials, through the use of CCA self-assembly, has motivated

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us to develop syntheses that easily and reliably prepare monodisperse, highly charged colloidal particles of different diameters. We have in the past successfully developed emulsion polymerization recipes for 100–400 nm diameter particles that form CCAs (50). These particles Bragg diffract light in the UV/vis/NIR regions of the spectrum.

In order to Bragg diffract light in the NIR region; the volume fraction of particles in the CCA must be very low. These dilute CCAs are more susceptible to disorder either by ionic contamination or shear forces. Due to the large array spacings, these dilute CCAs diffract light less efficiently. In order to overcome these problems, it is necessary to create CCAs from larger spheres. To our knowledge, there are no reports of the use of particles larger than 400 nm to create electrostatically stabilized CCAs.

Typically, emulsion polymerization cannot be used to produce monodisperse particles larger than 500 nm in diameter. The method of choice is a seeded polymerization where small monodisperse colloidal particles are used as the seed. The seed latex is swollen in a monomer solution, which is then polymerized within the particles resulting in larger, monodisperse particles. In addition to seeded polymerizations, emulsifier-free emulsion polymerizations can be used to obtain monodisperse particles larger than 500 nm in diameter (5–7, 11, 13, 15, 25–29, 31).

We describe here emulsifier-free emulsion polymerization recipes which produce particles of diameters between 500 and 1100 nm which efficiently Bragg diffract IR light. Our work has benefited from the numerous previous studies on the syntheses of monodisperse latex particles with surface charge groups (5, 15, 51–63), as well as from studies on the synthesis of monodisperse particles using emulsifier-free, emulsion polymerization techniques (5–7, 11, 13, 15, 25–29, 31).

EXPERIMENTAL

Synthesis

Styrene (Aldrich), 2-hydroxyethyl methacrylate (HEMA; Polysciences), sodium chloride (Fisher), and potassium persulfate (Aldrich) were used as received.

Monodisperse, highly charged poly[styrene-(*co*-2-hydroxyethyl methacrylate)] spheres were synthesized by emulsifier-free emulsion polymerization using a jacketed cylindrical reaction vessel (Kontes Model 612100, 613200), which contained a reflux condenser, and a Teflon stirrer, (Ace Glass Models 8093-22 and 5030-40), powered by a high-torque mechanical stirrer (Ace Glass Model 3584-10). The vessel also contained a temperature sensor (Ace Glass Model 12103-18) and a nitrogen/reagent inlet. The temperature was maintained through the jacket with the use of a circulating temperature bath (Fisher Model 13-265-5). The reaction vessel was charged with 205 mL of ultrapure water (Barnstead Nanopure water purification system) containing 70 g styrene, 2.0 g HEMA, and varying amounts of sodium chloride. A nitrogen blanket and a stirring rate of 350 rpm were main-

tained throughout the reaction. This solution was deoxygenated by bubbling with nitrogen for 1 h. After thorough deoxygenation, the temperature was increased to $70 \pm 1^\circ\text{C}$, and a solution of 0.11 g potassium persulfate in 5 mL of water was injected. The reaction was left to reflux for 24 h.

Upon completion of the reaction, the product appeared milky white. In reactions where little or no sodium chloride was added, the top of the liquid and the sides of the reaction vessel appeared opalescent.

After allowing the completed reaction to cool, the colloid solution was filtered through previously boiled glass wool and the filtrate was centrifuged into a pellet. The supernatant liquid was removed and pure water was added to the pellet, which was then sonicated to disperse the individual particles. This procedure was repeated until Bragg diffraction was observed (usually three repetitions). Ion exchange resin (Bio Rad mixed bed; AG501-X8, used as received) was added to the solutions for purification and storage.

Characterization

Particle sizes were measured using quasi-elastic light scattering (QELS; Brookhaven ZetaPALS) and transmission electron microscopy (TEM; Zeiss EM 902A). Optical diffraction measurements were performed by using a UV/vis/NIR spectrometer (Perkin Elmer Lambda 9). The particle charge densities were measured by conductometric and potentiometric titrations (64–66).

RESULTS AND DISCUSSION

Monodisperse, highly charged poly[styrene-(*co*-2-hydroxyethyl methacrylate)] colloidal particles with diameters between 500 and 1100 nm were synthesized using the recipes listed in Table 1. Obviously, the particle charge and diameter depend upon the reaction stoichiometry. All of these colloids readily form CCA, which exhibit sharp diffraction peaks in the NIR region, whose maximum diffraction wavelength depend upon the colloid concentration.

Figure 1 shows TEM micrographs of the synthesized highly charged, monodisperse spheres. The particles are spherical and relatively monodisperse up to diameters of ~ 900 nm, but above 900 nm, the particles become more polydisperse (Table 1).

The particle diameter increases as the reaction mixture ionic strength increases (67) (Fig. 2). This dependence on ionic strength occurs because the particles grow via a coagulation process. At low ionic strengths, the particles repel each other early in the reaction and do not collide and fuse into larger particles. At higher ionic strengths, larger particles are formed because increased charge screening allows more particle fusions. The particles repel each other only later in the reaction as they accumulate more surface charge; thus, a larger final diameter occurs. Particles above 1040 nm were not formed by these recipes due to the lack of colloid stability at very high sodium chloride concentrations.

TABLE 1
Particle Recipes, Diameters, and Surface Charge

Sample	Diameter (nm) ^a	Percentage polydispersity	NaCl (g)	Charges/Particle ($\times 10^5$)	Charges (nm ²)	Carboxylic acid groups/Particle ($\times 10^5$)	Charge density ($\mu\text{C}/\text{cm}^2$)
A	550	4.1	0	3.0	0.31	1.3	5.0
B	565	4.3	0	4.0	0.40	1.8	6.4
C	608	5.7	0.03	3.4	0.30	1.8	4.8
D	627	7.2	0.08	4.0	0.32	1.7	5.2
E	698	7.1	0.10	7.4	0.49	3.1	7.8
F	748	6.8	0.07	8.3	0.47	3.7	7.6
G	763	5.5	0.15	8.5	0.47	4.2	7.4
H	775	6.4	0.16	11.2	0.59	5.1	9.5
I	796	5.7	0.18	11.4	0.57	6.1	9.2
J	822	5.4	0.19	10.4	0.49	3.5	7.9
K	839	7.1	0.16	13.7	0.62	4.9	9.9
L	885	8.6	0.20	13.8	0.56	5.8	9.0
M	926	8.4	0.24	14.6	0.54	10.7	8.7
N	1040	9.8	0.30	14.5	0.43	9.4	6.8

Note. All reactions utilized: 70 g styrene, 2 g 2-hydroxyethyl methacrylate, 210 mL water, and 0.11 g potassium persulfate.

^a Diameters reported are from QELS measurements.

We previously demonstrated the synthesis of highly charged particles by adding an ionic comonomer during emulsion polymerization (50). However, we were not able to produce large particles using an ionic comonomer, either via emulsion polymerization or emulsifier-free polymerization. Instead of using an ionic comonomer for addition of charge to the surface, we have incorporated 2-hydroxyethyl methacrylate (HEMA), which has a primary hydroxyl group in its structure. HEMA polymerizes on the surface of the particles as shown by Galembeck *et al.* (68, 69). The primary hydroxyl group of HEMA is readily oxidized to a carboxyl group in the presence of persulfate, thus adding substantial charge to the surface of the particles (70). In addition to this weak acid group, we have increased charge on the

particles due to the attachment of the persulfate radicals to the particles' surface in the form of sulfate groups. While this half acid ester group can hydrolyze in water over time, we have not noticed any instability in our CCA over a 1-year period, possibly due to the large amounts of carboxylic acid groups on the surface (Table 1).

Figure 3 shows that the number of charges/particle increases with diameter (charges/particle were determined via conductometric and potentiometric titrations). For example, recipe B yields 565 nm spheres (Table 1) with $\sim 400,000$ charges/particle; recipe G yields 763 nm spheres with $\sim 850,000$ charges/particle; and recipe M yields 926 nm spheres with $\sim 1,450,000$ charges/particle. If the charge densities were constant, the number of

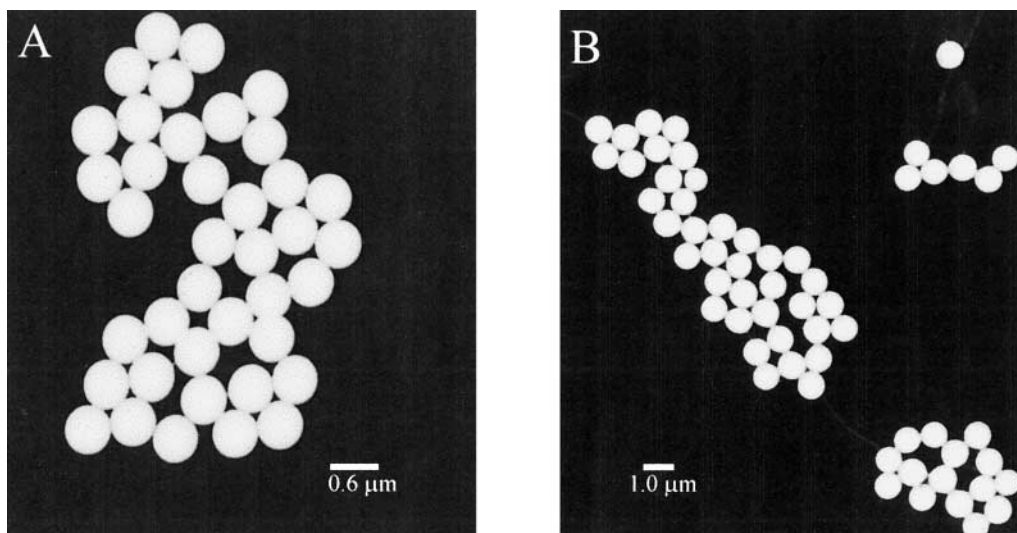


FIG. 1. TEM of the synthesized polystyrene particles. (A) 565-nm-diameter colloid (recipe B, Table 1), (B) 926-nm-diameter colloid (recipe M, Table 1).

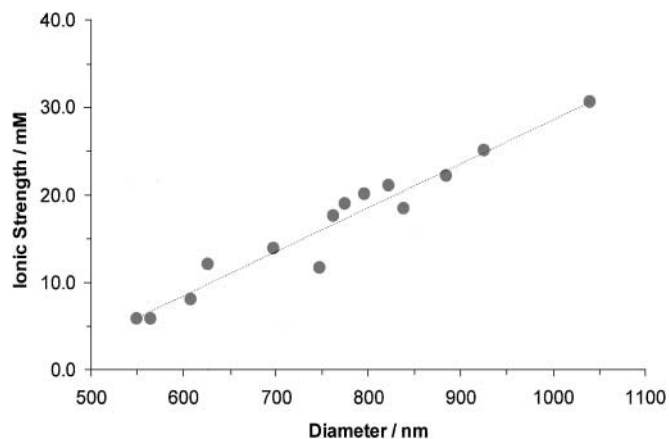


FIG. 2. Dependence of particle diameter on the ionic strength of the reaction mixture. (dashed line is the best fit).

charges/particle would increase with the square of the diameter. Figure 3 shows that the charge increases approximately as the square of the particle diameter. The inset of Fig. 3 moreover shows that the charge density increases slowly with particle diameter.

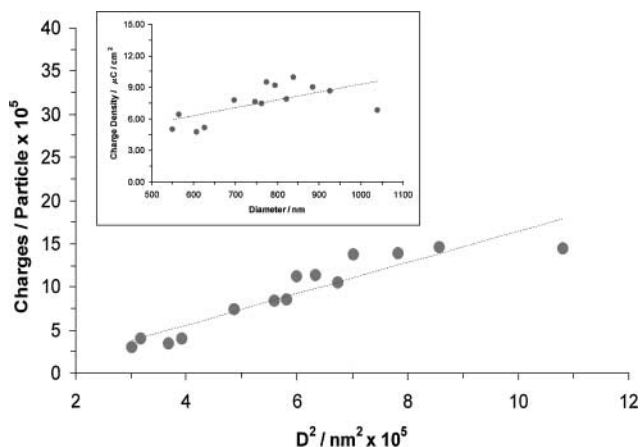


FIG. 3. Correlation between the number of charges/particle and the square of the particle diameter (dashed line is the best fit). (Inset) Correlation between the particle charge density and the particle diameter (dashed line is the best fit).

Figure 4A shows diffraction phenomena from the 111 planes of an FCC CCA. Figure 4B shows the angular dependence of Bragg diffraction from a 125- μm -thick CCA of 698 nm diameter colloidal particles. At normal incidence essentially all light

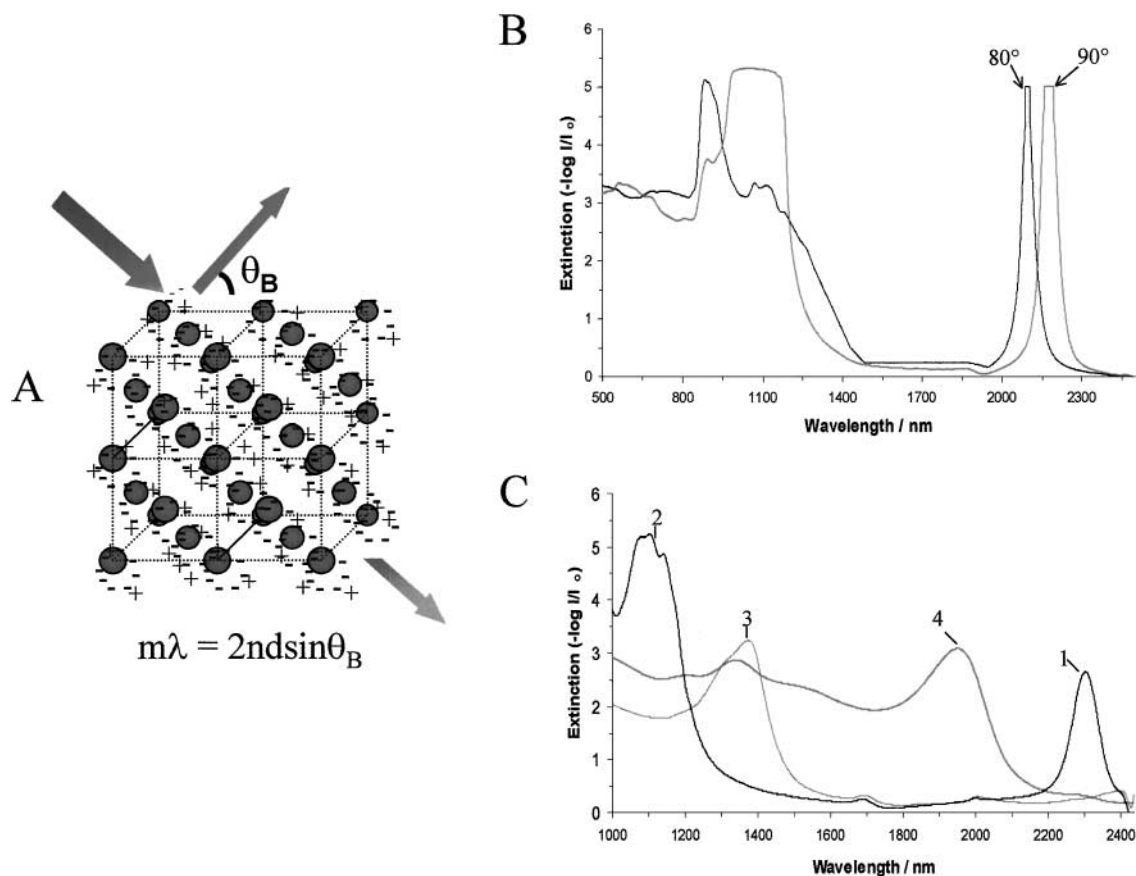


FIG. 4. (A) FCC CCA showing Bragg diffraction and the Bragg equation. (B) Diffraction spectra of CCA formed from 698-nm-diameter particles (recipe G, Table 1) at two different incident light angles. (C) Diffraction spectra of CCA from 698-nm-diameter particles at a lower particle volume fraction. Peak 1 is the primary diffraction peak of a CCA from the 698-nm-diameter particles; peak 2 is the secondary diffraction from same sample; peak 3 is the secondary diffraction peak from the 698-nm-diameter particles at an even lower volume fraction. The primary diffraction peak occurs at twice the secondary diffraction peak wavelength. Peak 4 is the secondary diffraction spectrum from a CCA of 926-nm-diameter particles (recipe M, Table 1) whose primary diffraction occurs at ~ 4000 nm.

meeting the diffraction condition at 2150 nm and at 1075 nm is diffracted. A tilt of the sample by 10° blue shifts the first-order diffraction, as expected from Bragg's law, while the second-order diffraction broadens and shifts as expected (38).

We were unable to measure first-order diffraction above 2700 nm due to water absorption. Although water absorption will limit the application of these photonic crystals for radiation filters past 2700 nm, this can be overcome by replacing the water in the samples with deuterium oxide or by simply polymerizing a polymer network around the CCA as we have previously demonstrated (49) and transferring this polymerized CCA to a solvent where absorption at the required wavelength does not occur.

The absorption of water in the 4000-nm spectral region results in a dramatically increased imaginary component of the material dielectric constant. This will serve to increase the extinction at all wavelengths within the water absorption band. Because of the periodicity of the water layers, the water absorption gives rise to a periodic variation of the imaginary component of the dielectric constant which also diffracts light. This will have a significant impact on the observed diffraction phenomenon. We expect changes in the diffraction efficiency and peak shape and width (34b). We hope to characterize these phenomena in the future when we construct instrumentation to directly measure the diffraction intensities.

We can estimate the first-order diffraction wavelength from the secondary diffraction (38) as shown in Fig. 4C. Peak 1 is the primary diffraction from a sample of 698 nm spheres, which has a nearest neighbor spacing of 865 nm. Peak 2 is the secondary diffraction from this sample, which occurs at half the primary diffraction wavelength. Peak 3, which was obtained from a lower volume fraction sample, is the secondary diffraction peak corresponding to primary diffraction at ~ 2800 nm. Peak 4 is the secondary diffraction peak (~ 2000 nm wavelength) from a CCA of 926 nm spheres which has a primary diffraction at ~ 4000 nm. The nearest neighbor spacing for this sample is 1504 nm.

We were unable to synthesize particles larger than 1040 nm diameter that formed robust CCA using procedures similar to those discussed above. The use of higher ionic strength resulted in essentially complete coagulation of the reaction solution. We are continuing our work toward developing syntheses of larger, highly charged monodisperse particles between 1 and 10 μm by using other polymerization techniques. We are also attempting to increase the surface charge on these poly[styrene-(*co*-2-hydroxyethyl methacrylate)] particles in order to obtain crystals which diffract further into the IR spectral region.

CONCLUSIONS

Recipes to prepare highly charged, monodisperse poly[styrene-(*co*-2-hydroxyethyl methacrylate)] particles of diameters between 500 and 1100 nm were developed. These particles readily self-assemble into robust three-dimensional CCAs that diffract light in the NIR region. By altering the volume

fraction of particles in the CCA dispersions, we are able to obtain wavelength tunable filters for all wavelengths between 1000 and 4000 nm as well as broad bands in the visible spectral region.

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