Colloidal crystals are unique building blocks for materials displaying complex nanoscale structures. The realm of architectures obtained through colloidal assembly may potentially be greatly expanded by utilizing two different types of colloidal particles. The controlled assembly of a binary system, however, requires the ability to tune interparticle interactions and to understand how these interactions affect the order of binary colloidal arrays. In this study we utilize two sets of monodisperse colloidal particles in the production of drop-coated array films: silica and polystyrene modified with amphoteric groups. The relative magnitudes of the surface charges on the two types of particles can be tuned continuously with pH, allowing for significant control over electrostatic interactions. Our results establish a correlation between the surface charge on the particles and the degree of order in the colloidal films that can be produced under different conditions. When both particles are highly charged, the particles self-assemble into polycrystalline close-packed arrays in which the two components are the result of mixed. More interesting results are obtained from binary arrays containing one weakly charged colloid, which will not order on its own, and a highly charged colloid. In this case, the highly charged silica particles act as a templating agent, forcing the weakly interacting polystyrene particles into an ordered crystalline lattice. Results for both low and high charge colloids can be explained on the basis of simple electrostatic calculations which show that the average interaction in a mixed system still favors ordering.

**Introduction**

Monodisperse colloidal particles of a variety of chemical compositions have the ability to crystallize into ordered arrays with a periodicity on the nanometer length scale. Colloidal crystals have also been used to create inverse opal structures via backfilling with ceramic, metal, or polymeric precursors with a goal of producing more complex and useful architectures. These materials have interesting potential applications as photonic devices due to the periodic variation of dielectric and their potential to show a photonic band gap. However, the use of a single type of particle limits the types of crystal structures that may be obtained. For example, for the FCC lattice, the most prevalent crystal structure in these systems, a complete photonic band gap appears only when the difference in dielectric constant between the particles and their surrounding material (typically air) is higher than about 3, a value that is difficult to achieve in the visible with most nonabsorptive materials. If more complex structures are desired, there is a need to utilize more complex building blocks by either changing the spherical shape of the colloidal particles or by utilizing more than one type of particle in a controlled assembly process. Nonspherical building blocks are difficult to manufacture in bulk quantities by a direct synthesis process but have been created by either elongation of spherical particles into ellipsoids or by joining two or more spherical particles that are constrained in lithographically patterned molds. Ordered arrays of elliptical shells have also been created in two steps starting from a colloidal crystal. There are numerous reports in which two populations of particles of the same composition but different sizes self-assemble from a bulk suspension over periods ranging from hours to months when left undisturbed. The structure of these lattices is a function of the relative size of the two types of particles, and they resemble the periodicities observed for some atomic systems. The particles utilized typically bear no surface charge and behave as hard spheres, however, limiting the ability to

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(2) Braun, P. V.; Wiltzius, P. Nature 1999, 402, 603.
control their self-assembly. In fact, while some of the phases observed in these binary hard-sphere systems are common to ionic systems, their phase diagrams show a strong dependence on subtle differences in relative concentration of the two types of particles. Simulations based on a cell method optimized for binary systems have confirmed the stability of many of the phases already observed experimentally. However, when the ratio of the two particle sizes approaches one-to-one, this work has failed to find a substitutionally ordered phase of formula AB, akin to the atomic structures observed in CsCl, NaCl, or ZnS.

Colloidal mixtures with different surface charges, related to our system, have been studied experimentally by other researchers. Several studies focus on the relative spatial correlation of two colloidal populations of different surface charge in a suspension and find that the populations are correlated in the liquid suspension, but that there is no evidence for formation of ordered colloidal crystals.

The phase diagram for colloids of the same size but with a variable amount of charge polydispersity has also been obtained through simulations. The results show that the ordered solid phase ceases to exist when the charge polydispersity exceeds about 30% and that under those conditions the stable solid phase is a glass. Recent simulations have focused on charge-bidisperse colloidal monolayers obtained by adsorbing particles of the same size onto an oppositely charged substrate. These theoretical investigations on colloidal mixtures with the same size but different surface charges suggest that, under conditions appropriate for each system, crystalline phases can exist. An experimental study of the coassembly of charged colloids of different compositions and interparticle interactions into binary arrays, however, has not been performed.

The focus of this work is to control the assembly of two different types of particles into a three-dimensional binary colloidal crystal and to elucidate the relationship between interparticle interactions and the order and structure displayed by the array after drying. We utilize two monodisperse sets of colloids of the same size: silica and polystyrene modified with ionizable groups that give it amphoteric character (APS). The sign and magnitude of the surface charge of the APS beads can be tuned continuously from positive to negative as a function of pH. As a result, the electrostatic interactions with the silica beads, whose charge is always negative in the pH range explored, may be tuned from strongly attractive to strongly repulsive.

The arrays were prepared by a drop-coating technique, which has been shown to produce ordered films of colloidal arrays. A small droplet of the suspension is allowed to evaporate on a substrate under controlled conditions to yield a thin film. Drop-coating has the advantage of producing films within a few hours as opposed to the weeks and months time scales often reported in crystallizing colloids from bulk suspensions. Over the short period of time required for the film to form, the suspension has good stability and is not likely to suffer contamination, which may in turn affect solutions parameter such as pH. In addition, the fast time scale of the experiment is particularly useful in binary systems as the two populations of colloids have different densities and tend to sediment at different rates, affecting the composition of the suspension.

**Experimental Section**

**Particle Synthesis.** Silica particles were prepared by the Stöber method with the following modifications. Tetraethoxy orthosilicate (TEOS) was hydrolyzed by small amounts of water in an ethanolic solution in the presence of ammonia. The reagents were mixed and stirred in a sealed plastic container for at least 3 h at room temperature. The amounts of water and ammonia present in solution regulate the rates of nucleation and growth for the particles and ultimately affect their final size. We found that the use of appropriate amounts of ammonia dissolved in ethanol instead of ammonium hydroxide produced particle populations with better size distributions. Seed particles were grown to the desired diameter by successive additions of TEOS and water in a 1:2 mole ratio. This procedure can be used to both increase the average colloid size and to narrow the size distribution of the population. TEOS was distilled under vacuum before use.

Amphoteric polystyrene (APS) particles were prepared by slight modification of a literature method. In a typical synthesis 2.00 g of (diethylamino)ethyl acrylate (DEAM) and 1.00 g of methacrylic acid (MA) corresponding to a 1.1 mole ratio, were mixed and dissolved in about 230 mL of an aqueous solution of hydrochloric acid of pH 1.2. About 20 mL of styrene was added with vigorous magnetic stirring to emulsify the mixture. After the emulsion was heated to 75 °C, the polymerization was initiated by adding 0.40 g of potassium persulfate dissolved in about 20 mL of water. The reaction was allowed to proceed under heating and vigorous stirring for 24 h. The stabilizing inhibitors added by the manufacturer to styrene and methacrylic acid were removed just before use by means of the appropriate disposable prepackaged purification columns available through Aldrich. DEAM was distilled under vacuum. All reagents were purchased from Aldrich. We found that the use of freshly purified reagents is required to obtain monodisperse populations and that for this purpose it is also useful to carry out the polymerization in an oxygen-free environment.

For this work, monodisperse APS particles with an average diameter of 252 nm and a standard deviation of 2.0% were prepared. A seed dispersion of silica particles was step-grown to match the size of the APS population. The silica sample had an average diameter of 249 nm with a standard deviation of 4.0%.

**Particle Purification.** Silica particles were purified by several cycles of centrifugation and resuspension. Absolute ethanol was used initially, and Milli-Q water was used in the final stages. Particles were then dialyzed several times in an Amicon ultrafiltration cell containing a fine nylon mesh to remove coarse coagulate and then quickly extracted with hexanes to remove most of the unreacted monomer and oligomers. The water phase was then extensively dialyzed in an ultrafiltration cell in concentration mode. To optimize the purification, the particles were resuspended in different media at the end of each dialysis cycle. For the first several cycles dilute hydrochloric acid was used; this was followed by several cycles where the particles were resuspended in dilute sodium hydroxide. As only uncharged oligomers are effectively dialyzed out in an ultrafiltration process, this technique allows one to eliminate
molecules that are uncharged at different pH conditions. Sodium and chloride ions were finally removed by using Milli-Q water as the suspending medium for several cycles. The residual monomer odor was eliminated by bubbling steam through the suspension for 2 h. Finally the particles were stirred in the presence of a mixed-bed ion-exchange resin to a constant conductivity reading.

**Particle Characterization.** Calculation of size and size distribution for the population was obtained from the purified products by measuring the size of at least 100 particles in TEM micrographs obtained using a j oel 100CX microscope.

The ζ-potential of the particles was measured on a Pen Kem, Inc., Lazer ZeeMeter model 501 using deionized solutions whose pH was adjusted to the desired value with dilute HCl or NaOH.

The particle concentration as a volume percent of the purified solutions was estimated from the density of silica (2.2 g/mL) and APS (1.05 g/mL) using a dry-out method.

**Film Deposition.** All solutions were prepared using degassed Milli-Q water, which was stored over a mixed bed ion-exchange resin. The suspensions were 0.5% volume fraction in particles. The binary suspensions were 0.25% in each silica and APS. The solutions were prepared under inert atmosphere to minimize contamination by atmospheric CO₂. The pH was adjusted with NaOH volumetric standards.

The cells for drop-coating were prepared by adhering a small piece of a 3 mm thick sheet of paraffinic wax with a circular hole to a warm substrate. The 6 mm diameter hole was punched into the wax before placing onto the substrate and serves the function of containing the suspension droplet during evaporation. A 40 μL drop of the suspension was placed in the hole on the substrate and allowed to evaporate in an argon atmosphere with relative humidity of no more than 20%. The wax could be peeled off after the film was dry.

Silicon wafers were used as substrates for samples to be imaged by scanning electron microscopy, and glass microscope slides were used for the UV–vis experiments. All substrates were cleaned in a chromic/sulfuric acid bath, rinsed well with Milli-Q water, and dried at 80 °C.

**Film Characterization.** Films formed from suspensions at low pH (where attractive interactions dominate) appear clumpy and uneven. Films produced at slightly higher pH appear uniform over the entire circular area and frequently showed iridescent behavior under direct lighting.

Scanning electron micrographs of the films were obtained on a Philips XL-30 equipped with a field emission source. No coating of the samples was necessary for films grown on silicon substrates. This allows us to distinguish silica (lighter particles) from APS (darker particles) in the micrographs of binary films. Energy dispersive X-ray (EDX) analysis was carried out using the SEM and probing regions of the film of roughly 5 × 5 μm². A maximum accelerating voltage of 15 kV was used to probe the elemental composition of the film only, avoiding the substrate. This value of accelerating voltage is believed to probe most of the film thickness for the particular type of APS bead. The lack of any substantial amount of stabilizing surface charge under these conditions is confirmed by the experimental observation that exhaustively deionized solutions of APS show very poor stability and begin to sediment within minutes.

When the pH is lower than about 6, most of the amine and carboxylic acid functionalities are protonated and the particles have a net positive charge. The magnitude of this charge increases as the pH is reduced as a larger fraction of the carboxylic acid groups become protonated. Conversely, when the pH is raised above 7, the ζ-potential is found to be increasingly negative as more and more ammonium groups undergo deprotonation. The stability of these suspensions at pH less than 6 and more than 7 is excellent with no observable sedimentation over the course of many months.

The ionization of silica particles is simpler as it is merely controlled by the weakly acidic behavior of the silanol group. A fraction of the silanol groups is always ionized (above pH 2) resulting in increasingly negative ζ-potential values with increasing pH. An exhaustively deionized silica suspension has a pH between 4 and 6 depending on the volume fraction of particles and is stable over long periods of time because of its substantial surface charge.

The APS copolymer contains a large number of carboxylic acid and tertiary amine residues. Any of these groups that are near the particle surface have the ability to participate in ionic equilibria and thus to vary the net surface charge of the particles as a function of pH. Consideration of the relative acidity of carboxylic acid and ammnium groups leads us to believe that, in an exhaustively deionized solution, ionic equilibria favor a zwitter-ionic balance between the deprotonated carboxylate residues and the protonated ammonium groups. As the mole ratio of these negatively and positively charged groups is about 1, the overall surface charge and ζ-potential are thus close to 0 under completely deionized conditions. This corresponds to pH values near neutral, which we designate as the isoelectric point of this particular type of APS bead. The lack of any substantial amount of stabilizing surface charge under these conditions is confirmed by the experimental observation that exhaustively deionized solutions of APS show very poor stability and begin to sediment within minutes.

Results

To understand the types of interaction between the two populations of colloids, measurement of their surface charge as a function of pH is necessary. This is related to the ζ-potential, the electrostatic potential associated with the net charge on the surface of a colloidal particle, which can be measured easily by electrophoretic methods. The ζ-potential was measured by preparing dilute solutions of each of the particles over a wide pH range. These data are presented in Figure 1.

**Figure 1.** pH dependence of the ζ-potential for silica (△) and APS (○) particles. The surface charge of the silica particles is negative at all the pH values explored in this work, whereas the surface charge of APS may be tuned from positive to negative as the pH is increased.
ably as a function of pH. At pH values lower than about 5, APS and silica are oppositely charged and experience a strong electrostatic attraction. This results in the very rapid formation of randomly shaped conglomerates of macroscopic size which sediment quickly. This regime is referred to as heterocoagulation\(^{32}\) and is not useful when trying to form ordered colloidal arrays. At pH values near neutral, the interaction between silica and APS is very weak due to the low charge on the APS. As the pH is increased both particles become negatively charged and form a stable suspension. Uniform films with no macroscopic coagulates can be formed under any conditions where the APS colloids are neutral or negatively charged.

Binary films were grown at three different conditions: exhaustively deionized conditions; at a pH value of about 7 and at a pH value of 8.5. For the higher pH cases, the pH was adjusted with an appropriate amount of NaOH. In the rest of this work we refer to these conditions as deionized, low-base, and high-base. To draw comparisons between these binary films and the structure of pure films of silica and APS particles, the pure films were also grown under the same three sets of conditions. Figure 2 summarizes the experimental conditions used in this work and includes an estimate of the value of the ionic strength of the suspension. This is associated with a decrease of the Debye screening length and of the range of interparticle interactions.

Figure 2. Sample suspension conditions for film deposition. Silica samples are shown with triangles, APS samples with squares, and binary samples with circles. The empty symbols represent deionized conditions; the gray symbols correspond to low-base conditions, and the black ones to high-base. The addition of base increases the surface charge of the colloids as well as the ionic strength of the suspension. This is associated with a decrease of the Debye screening length and of the range of interparticle interactions.

Figure 3. Absorbance spectra of the film samples. For each of the three conditions, the three traces represent silica, binary, and APS films, respectively, in order of increasing wavelength for the peak position. The increase in peak wavelength is correlated with an increase in the average index of refraction of the colloids in the film. In all cases the background has been subtracted and the intensities have been normalized. It is 545 nm; the binary films have an intermediate value of 525 nm.

Figure 4 shows SEM images representative of the nine samples. The general trend shows an increasing degree of order as the pH of the original suspension is increased. This behavior is barely noticeable for pure silica films, which show good order even under deionized conditions. The trend is more apparent for binary films and very marked in the APS films. For the APS films, the order varies continuously from a disordered structure resembling a glass under deionized conditions to a polycrystalline film of (111) orientation at the highest pH. Numerous domains of (100) orientation and accompanying lattice defects are also present. In binary films, silica and APS particles are discernible as bright and dark particles, respectively.

To quantify the degree of order of our samples as observed by SEM, the images were processed using a fast Fourier transform (FFT) algorithm (Figure 4, insets). The rings, as opposed to spots, in the FFT images are due to the polycrystallinity of the films. By analogy with the analysis of X-ray diffraction patterns, the intensity of these rings was angularly integrated and generated a plot of intensity as a function of scattering vector. This intensity contains two components: The first is the analogue to incoherent scattering due to the intrinsic length scales present in the sample and is similar to what is seen in conventional small-angle X-ray scattering. The second is the analogue of coherent scattering or Bragg scattering and contains information about any periodic structure of the sample. As we discussed, the APS deionized sample shows no order and consequently the integrated intensity for this sample contains only incoherent scattering. This

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sample was therefore utilized as a reference; its incoherent signal was subtracted from the integrated intensity of all other samples to extract the information about the periodicity of the samples. The patterns obtained in this fashion (from ordered films) index to a 2-dimensional hexagonal pattern (plane group $p6m$), as expected for

**Figure 4.** SEM images of the nine samples. Deionized conditions are shown in the first row for silica (a), APS (b), and the binary film (c). Low-base conditions are in the second row for silica (d), APS (e), and the binary film (f). High-base conditions are shown in the third row for silica (g), APS (h), and the binary film (i). The side of each square image is 10 µm. FFT's obtained from images at lower magnification are shown in the insets. In general the order of the films improves as the interparticle interactions become more repulsive. Binary films, however, show significantly better order than pure APS films under deionized or low-base conditions.

**Figure 5.** Fitting to the integrated intensity of the FFT images from Figure 4 for (a) deionized, (b) low-base, and (c) high-base conditions. In each case the silica, APS and binary samples are shown from top to bottom. The noisy line represents the experimental data; the gray traces are Gaussian peaks fit to the data, and the black smooth lines represent their sum corresponding to a $p6m$ hexagonal pattern. No experimental data are available for the APS deionized case, as this completely disordered sample was used as a reference (see text). Under deionized and low-base conditions, the highly charged silica particles act as a template, inducing APS particles to close-pack, despite the fact that APS particles show no ability to order by themselves at deionized or low-base conditions.
Figure 6. Degree of order in the sample presented as quality of fit for the integrated intensities shown in Figure 5. The degree-of-freedom adjusted factor of correlation is plotted to account for differences in the number of data points fit for each sample. As in Figure 5, no data are available for the APS deionized sample because it represents the reference for all others. The order for the silica HB sample is slightly lower than the other two silica samples probably due to high values of ionic strength (see text). The APS films have little or no ability to order under LB conditions but do display order comparable to that of silica at HB conditions. The order of the binary films increases monotonically as the pH of the solution increases.

The (111) face of a cubic closed-packed structure. Figure 5 shows the result of this analysis for all nine samples. The first 4 peaks of the pattern were fit with Gaussian curves of the same width whose centers have relative values appropriate for a hexagonal pattern (1:√3:2:√7).

The quality of the fit to the hexagonal pattern is an indication of the degree of order in each of the films. In Figure 6 the quality of fit is quantified using the degree-of-freedom adjusted $R^2$ for all samples. This version of the coefficient of determination for the fit to experimental data allows a more meaningful comparison of data sets that do not contain the exact same number of data points, as in our case. The results indicate that all silica films and high-base APS films can be reasonably fit with a hexagonal function. Deionized binary films show only moderate order, but the integrated radial distribution functions from low base and high base binary films are well approximated with a hexagonal function. Low-base APS films do not appear to be ordered and cannot be fit with a hexagonal scattering function.

Discussion

In systems of a single type of particle, the amount of surface charge of the particles and the ionic strength of the suspension affect the crystal structure of colloidal crystals in equilibrium with a fluid phase. In general, dilute suspensions of highly charged particles may originate a BCC crystal as a consequence of their long-range interactions. FCC crystals tend to form from more concentrated suspensions. The ionic strength of the suspension also plays a central role as free ionic charges in solution cause condensation of counterions onto the highly charged particle surfaces, substantially decreasing their effective charge. As the effective charge is reduced, the interparticle interactions may start approaching hard-sphere behavior, favoring a closed-packed structure in the crystalline phase.

The colloidal arrays produced through drop-coating techniques form upon solvent evaporation. In addition to interparticle electrostatic interactions, the strong capillary forces associated with solvent evaporation thus tend to pull particles together, encouraging the formation of a close-packed structure. The films grown by this technique are also clearly formed under conditions of high particle concentration, which is another factor favoring close-packed structures. However, the value of ionic strength in binary colloidal suspensions is still important because screening of the surface charge by free ions can modify the interparticle interactions during the assembly process. As the solvent evaporates and the ionic strength increases, these electrostatic interactions become more short ranged.

At the same time, however, solvent loss decreases the average particle–particle spacing. Our low-base and high-base samples are prepared by addition of controlled amounts of sodium hydroxide to the suspensions to achieve the desired pH. The addition of hydroxide ions partially titrates the acidic surface groups resulting in an increase of the suspension pH and thus an increase in ionic strength and a decrease of the Debye screening length. The sodium ions also contribute to an increase of the ionic strength of the solution.

The ionic strength of the solution from which our samples were prepared (indicated in Figure 2) was calculated by utilizing conductivity measurements on the suspensions. It was assumed that the only ionic species contributing to diffusive conductance and to the total ionic strength were hydronium, hydroxide, and sodium ions. The sodium ions were assumed to undergo partial ion condensation on the surface particles and to be present as free ions at 90% of their nominal concentration. This assumption is consistent with previous work on conductance of charged colloidal suspensions. Approximately a 10-fold increase in ionic strength is observed between each of the pH conditions (Figure 2). Solely on the basis of the ionic strength, we would expect to find the poorest order at the highest ionic strength conditions (i.e. high-base) because of shielding of electrostatic repulsion between colloids and counterion condensation (i.e. a reduced Debye screening length). The results presented in Figures 4–6 suggest that the opposite trend is frequently observed and so differences in ionic strength between the various conditions are not dominantly responsible for the trends observed in the data.

The order displayed by the nine samples (Figures 4–6) is a function of pH and surface charge. Sufficient repulsive interactions are required for the colloidal particles to organize in a close-packed structure. Silica particles have a substantial amount of charge throughout the pH range explored in this study resulting in good order under all conditions. The slighty poorer order displayed under high-base conditions (visible in Figures 4g and 6) is most likely associated with the high value of ionic strength for this

\[(35) \text{The definition of the DOF adjusted factor of correlation is}
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\[R^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{(n - m - 1) \sum_{i=1}^{n} (y_i - \bar{y})^2} \]

where $\hat{y}_i$ is the fitted value for the experimental value of $y$, $\bar{y}$ is the average of $y$ for all $n$ data points, and $m$ is the number of parameters fitted (six in our case).

\[(36) \text{Dhont, J. \& G. Smits, C.; Lekkerkerker, H. N. W. J. Colloid Interface Sci. 1992, 152, 386.}\]

\[(37) \text{Okubo, T. J. Colloid Interface Sci. 1998, 125, 380.}\]

\[(38) \text{Quesada-Perez, M.; Callejas-Fernandez, J.; Hidalgo-Alvarez, R. J. Colloid Interface Sci. 2001, 233, 280.}\]
sample.\textsuperscript{18} In fact, preliminary experiments show that the ability of silica particles to order into colloidal arrays is inhibited completely by the addition of as little as 1 mM sodium chloride.

The trend of increasing order with pH is most evident for the APS films. The surface charge on the APS particles increases dramatically from near zero under deionized and low-base conditions to a charge comparable to that of silica at high-base concentrations. This translates into films that show no order under deionized conditions and to ordered, close-packed film under high-base conditions.

Binary films show a behavior that is intermediate between the behaviors of the two components. A continuous increase in order is present as the pH of the solution is increased and the interparticle interactions become more repulsive. This is difficult to fully appreciate from the images of Figure 4 but is more obvious when the quality of fit is compared in Figure 6. While the specific $R^2$ values are not as high as those observed for silica films, they are significantly higher than the value obtained for the disordered APS film, and thus they indicate a reasonable degree of ordering in the binary films. It should also be pointed out that the reported $R^2$ values for the fits in the case of the binary films should to be considered lower bounds because the different levels brightness for silica and APS particles in the original micrographs are expected to introduce inhomogeneity when the image is processed using an FFT routine.

These results indicate that the silica particles act something like a template in the binary films. This is most evident for the low-base conditions (Figure 5b): highly charged silica particles induce the formation of an ordered binary film under conditions where the pure APS particles completely fail to organize into an ordered array. While the silica sample shows a clear hexagonal pattern with four clearly indexable peaks, the APS film is characterized by a complete lack of long-range periodicity as demonstrated by a value of $R^2$ lower than 0.60 (Figure 6). The signal from the binary film is satisfactorily fitted by four peaks indexing to a hexagonal pattern, just like in the case of silica.

**Film Composition.** In the formation of the binary films, colloids were mixed in a 1:1 ratio of silica and APS particles. All binary films show comparable amounts of light (silica) and dark (APS) particles. When clearly distinguishable particles are counted on the SEM micrographs, the volume fractions are 54% for silica and 46% for APS; these values vary slightly from one region of the film to the next, and the error associated with them is about 10%. EDX signals were also collected to measure to composition of the binary films. Analysis of the C to O ratio integrated over a 5 $\mu$m$^2$ area reveals that the volume fraction is indeed (50 $\pm$ 2)% for both components for all three binary films. As a complement to the SEM images, the distribution of silica and APS was also analyzed locally through EDX mapping of a low-base binary colloidal film (Figure 7). The best resolution was achieved for lower accelerating voltages and is estimated to be no better than 0.5 $\mu$m for carbon and oxygen and somewhat larger for silicon. The signal is thus averaged over adjacent particles resulting in variations from uniform elemental abundance only when several particles of the same kind happen to be clustered. The images show intensity variations on the length scale of the spatial resolution, again indicating good mixing of the colloids. A few larger (though not completely homogeneous) domains on the order of 1–2 $\mu$m can be observed, but the results generally indicate good mixing of the polymer and silica colloids down to very small length scales.

![Figure 7. EDX mapping images of binary low base films: (a) direct imaging of the sample surface by secondary electron detection, where light particles are silica and dark particles are APS; EDX map for (b) carbon, (c) oxygen, and (d) silicon. Light areas correspond to higher concentrations for each element. Variations in the elemental composition are only visible when several particles of each kind are close together because the resolution of the EDX is larger than the size of a single particle. These data suggest that silica and APS particles are thoroughly mixed on the 1–2 $\mu$m length scale.](image)

While SEM and EDX data provide information about the top surface of the films through direct imaging, UV–vis absorbance experiments of the films complement these data by sampling the periodicity in the direction normal to the substrate. The absorption peak is associated with diffraction of visible light with wavelengths satisfying the Bragg condition along the axis of propagation.\textsuperscript{33} At normal incidence to the film, the peak position occurs at $J_{\text{max}} = 2\sin(\theta/2)\lambda$, where $\lambda$ is the spacing between (111) layers in a close-packed structure and $n_{\text{eff}}$ is the effective refractive index of the film. In a close-packed lattice, $d_{\text{111}} = (2/3)D$, where $D$ is the particle diameter and $n_{\text{eff}} = (74\%n_{\text{particle}}^2 + 26\%n_{\text{air}}^2)^{1/2}$. Figure 3 shows the absorption peaks after background subtraction. As the interlayer spacing is expected to be the same for all types of films, the difference in peak position reflects differences in the effective indexes of refraction of the material. While the intensity of the peaks is related to the degree of order in the films as seen by SEM, the peak position is the same for silica, APS, and binary films across the three types of conditions explored. This is to be expected, as only the ordered portions of the film would contribute to a signal due to Bragg scattering. From the peak position of the pure films the index of refraction for the silica and APS particles can be calculated to be 1.327 and 1.422, respectively. The value for silica is slightly lower than the value of 1.375 reported by Bertone et al.\textsuperscript{3} This small difference may be due to some porosity in the silica particles as a consequence of our step-growth process. Titration experiments performed on these samples have confirmed a slightly porous structure for these silica particles, which would produce a lower value of $n$. We are unaware of any reports on the index of refraction for latexes similar to our APS particles. Pure polystyrene has an index of refraction of 1.498\textsuperscript{39} but contains a higher proportion of aromatic groups. From the peak position of the binary films and the values of $n$ for silica and APS obtained from the pure films, the composition of the binary films can be calculated.

The DLVO plots also allow us to understand general trends in film ordering. Plots of interaction energies for the low-base conditions show that the silica–APS interaction is strongly repulsive while the APS–APS interaction is only barely repulsive. This accounts for the observation that, under low-base conditions, the pure APS film does not order but that the mixed film does. Under high-base conditions all interactions are repulsive and the magnitude of surface charge is more similar for the two types of particles, resulting in reasonable order for both pure and binary films (Figure 6).

Analysis of the relative arrangement of silica and APS films in micrographs of binary samples reveals that any given crystal lattice point is occupied by either silica or APS particles with the same probability. By careful inspection of the micrographs it is found that when like-nearest-neighbor pairs of particles are counted, both silica and APS particles have roughly the same probability to be adjacent to a like particle as they do to a particle of the other kind. In other words, there is complete substitutional disorder in the crystals and no correlation between the position of silica and APS within the lattice.

Ideally, the mixing predicted by DLVO theory would be most efficient between the two components in a binary film if they were arranged into two interpenetrating simple cubic lattices, as seen in ionic solids such as calcium chloride. Therefore, it seems that by predicting that mixing is always favored, DLVO theory would dictate that our colloidal arrays should be a positionally ordered crystalline phase in which the relative position of the two types of particles are correlated. This positionally ordered state would be most favored when the energy difference between the silica–APS pair and the average of the silica–silica and APS–APS interactions is greatest. This corresponds to our samples at lower pH (Figure 8). However, this tendency to form a substitutionally ordered crystal as the pH is lowered is not observed experimentally in our binary films, possibly for kinetic reasons.

In a recent investigation into the ability of a charge-bidisperse system to order, Gray et al. theoretically explored the structure of a 2-dimensional system formed by the adsorption of two colloids with different amounts of surface charge onto an oppositely charged substrate. The conditions of their simulations are similar to our experiments, and their conclusions are that even when ordered monolayers are obtained, their system fails to generate a binary lattice with positional order due to kinetic limitations.

Although a large difference in surface charge should favor binary ordering on the basis of our DLVO calculations, it is not expected to be advantageous for positionally disordered systems such as the ones presented here. Tata et al. examined crystallization in charge polydisperse systems (as opposed to our charge bidisperse systems). Their simulations show that the stable solid phase changes from a crystal to a glassy state when the charge polydispersity exceeds 30%. In agreement with this, under high-base conditions, when the charges on silica and APS are similar and the value of polydispersity is below the threshold value of 30%, we find good crystalline order. However, at low-base and deionized conditions, as the polydispersity increases, the order in the binary films decreases and moves toward a slightly more glassy state (Figure 6).

The DLVO plots also allow us to understand general trends in film ordering. Plots of interaction energies for the low-base conditions show that the silica–APS interaction is strongly repulsive while the APS–APS interaction is only barely repulsive. This accounts for the observation that, under low-base conditions, the pure APS film does not order but that the mixed film does. Under high-base conditions all interactions are repulsive and the magnitude of surface charge is more similar for the two types of particles, resulting in reasonable order for both pure and binary films (Figure 6).

Analysis of the relative arrangement of silica and APS films in micrographs of binary samples reveals that any given crystal lattice point is occupied by either silica or APS particles with the same probability. By careful inspection of the micrographs it is found that when like-nearest-neighbor pairs of particles are counted, both silica and APS particles have roughly the same probability to be adjacent to a like particle as they do to a particle of the other kind. In other words, there is complete substitutional disorder in the crystals and no correlation between the position of silica and APS within the lattice.

Ideally, the mixing predicted by DLVO theory would be most efficient between the two components in a binary film if they were arranged into two interpenetrating simple cubic lattices, as seen in ionic solids such as calcium chloride. Therefore, it seems that by predicting that mixing is always favored, DLVO theory would dictate that our colloidal arrays should be a positionally ordered crystalline phase in which the relative position of the two types of particles are correlated. This positionally ordered state would be most favored when the energy difference between the silica–APS pair and the average of the silica–silica and APS–APS interactions is greatest. This corresponds to our samples at lower pH (Figure 8). However, this tendency to form a substitutionally ordered crystal as the pH is lowered is not observed experimentally in our binary films, possibly for kinetic reasons.

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The DLVO theory thus predicts that mixing is always favored, which should result in a crystalline phase with binary positional order. In the absence of binary ordering, however, examinations of charge polydispersity suggest that a glassy state should be produced at the lower pH.

Figure 8. Energy calculations for interparticle interactions based on DLVO theory at (a) deionized, (b) low-base, and (c) high-base conditions. In each case from top to bottom the four traces represent the binary interactions between the following pairs of particles: silica–silica, average (see Discussion); silica–APS; APS–APS. The difference in axis scale between the three plots reflects the increase in ionic strength and the shortening of the screening length as the pH is increased. The average interaction is always more repulsive than the silica–APS interaction, which explains the good mixing observed in these systems. Under low-base conditions in part b, the binary interaction is moderately repulsive (which favors ordering) while the APS–APS interaction is almost neutral (which leads to a disordered or glassy film).

Electrostatic Calculations. The thorough mixing of silica and APS particles in binary films may be understood using calculations of the energy of interaction between particles based on DLVO theory. This theory allows one to calculate the energy profiles as a function of separation whenever the potentials, the sizes of the particles, and the ionic strength of the solution are known, as in our case. In a recent attempt to correct for the pairwise additivity approximation in DLVO theory, Kwon et al. carried out energy calculations for different clusters of colloidal spheres of the same kind. Their findings confirm that DLVO calculations provide good estimates of interaction energies under the conditions of our experiments.

In our binary suspension, three different pair interactions are present: silica–silica; APS–APS and silica–APS. The most striking result of the calculations presented in Figure 8 is that the energy of interaction between silica and APS is smaller than the average energy of interaction for the two like pairs at all separations for all conditions explored in our experiments. DLVO theory therefore predicts that mixing of silica and APS is always favored over phase separation. This is consistent with our SEM micrographs, EDX data, and absorption measurements, all of which show good mixing of silica and APS in the binary films. Careful examination of Figure 7, however, may suggest slightly more clustering of the APS colloids than the silica colloids in binary films made under low-base conditions. This result is also in agreement with our DLVO calculations. While the silica–silica interactions are highly repulsive, the APS–APS interactions are only barely repulsive in comparison to KT. Mixing of the entire system is thus driven by mixing of the silica colloids, a situation that allows some small APS domains to exist.

The DLVO theory thus predicts that mixing is always favored, which should result in a crystalline phase with binary positional order. In the absence of binary ordering, however, examinations of charge polydispersity suggest that a glassy state should be produced at the lower pH.
values used in our experiments. Neither of these results are experimentally observed, but an understanding of our data can be obtained if we consider the capillary forces associated with solvent evaporation, which provide an additional incentive for close packing. In our system, the growth of films is neither slow nor reversible, as seen in experiments in which a crystalline phase slowly forms from a bulk colloidal suspension. We believe this may be part of the reason we observe no positional order. While capillary forces provide a strong driving force for close packing, they are short range and unidirectional, and thus, they do not favor positional ordering. While electrostatic interactions may favor positional ordering, the thermal energy available to the system and the large size of the colloids make rearrangements of this magnitude kinetically impossible. Therefore, for this system the substitutionally disordered close packed state observed experimentally represents the only accessible final configuration available for the particles.

**Conclusions**

This study explores the correlation between the order displayed by binary colloidal crystal arrays formed by drop-coating and the interparticle interactions in the suspension from which they are formed. It is found that repulsive interactions are associated with better order and result in polycrystalline close-packed films in which the two types of particles, silica and polystyrene, are thoroughly mixed. It is also found that highly charged silica particles act as a templating agent, forcing the weakly interacting polystyrene particles into an ordered crystalline lattice, despite the fact that the pure polystyrene particles will not order by themselves under these conditions.

Understanding the relationship between electrostatics and self-assembly in colloidal systems represents a key step in controlling the formation of colloidal arrays with specific structures. The findings of this study should prove useful in planning the self-assembly of new materials with complex three-dimensional architectures through colloidal templating.

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