Controlling Porosity within Colloidal Heteroaggregates

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Heteroaggregates of cationic poly(2-vinylpyridine) microgels and anionic polystyrene latex particles have been made by mixing dilute, aqueous suspensions. The growth of the heteroaggregates was arrested by the addition of anionic silica particles that adsorbed to the free surface of the cationic microgel particles. The resulting heteroaggregates were then concentrated by vacuum filtration, freeze-dried, and characterized by mercury porosimetry and electron microscopy. The inclusion of soft, deformable microgels resulted in heteroaggregates with higher porosity than obtained with heteroaggregates of anionic and cationic latex particles. Control of the pore volumes within the freeze-dried filter cakes was demonstrated by two approaches. In the first approach, heteroaggregation at a constant KCl concentration of 0.01 mM was arrested at different times after mixing the latex and microgel particles, thereby limiting the size of the aggregates. The porosity of the resulting filter cake increased from 61 to 65 vol % as the aggregation time increased from 15 to 120 s. In the second technique, the aggregation time prior to arrest was maintained at 120 s while the KCl concentration was varied between 0.01 and 10 mM. The pore volume of the aggregates decreased from 65 to 57 vol % as the electrolyte concentration increased, a trend explained in terms of the effect of the Debye length on the aggregation process.

Introduction

Synthetic materials with high porosity (>50% v/v) are used in a large variety of applications including supports for solid-phase synthesis1 and biological tissue growth,2 absorbent pads,3 sensors,4 and printing.5 In some applications, such as filtration and chromatography,6 the control of the pore size is critical. Heteroaggregates with low fractal dimensions are potentially highly porous,7,8 and heteroaggregation of oppositely charged colloidal particles of similar size can produce aggregates with low fractal dimension (d < 1.8) that have open structures.9,10 Nevertheless, recent studies of heteroaggregates with oppositely charged particles of similar size have focused on the rate of aggregation and the fractal dimension of the aggregates.5–14 The porosity of colloidal heteroaggregates produced using oppositely charged particles has rarely been studied. An exception to this is the work of Tang et al.15–17 Tang and co-workers demonstrate control of pore size and porosity through the ratio of particle types and size of the particles,15–17 the method requires high-temperature calcination and results in spherical pores in an inorganic matrix of smaller particles. By contrast, heteroaggregation of similarly sized particles at low electrolyte concentrations, form chainlike structures of alternating particle types in solution10 and do not have spherical pores.

The fractal dimension of heteroaggregates produced from oppositely charged, similarly sized particles can be controlled by electrolyte concentration,10,12 which alters the range of electrostatic interactions between particles. Theoretically, increasing the porosity of heteroaggregates can be achieved by lowering the fractal dimension or increasing the size of the aggregate,7,8 however there do not appear to be any examples in the literature where the effect of electrolyte concentration or aggregate size on porosity is measured.

In the current study, the pore size and total pore volume of freeze-dried heteroaggregates are investigated by mercury porosimetry, a standard method for characterizing porous materials. The control of porosity within aggregates is explored by adjusting both the heteroaggregate size and the electrolyte concentration during the aggregation process. Control over the size of heteroaggregates is attempted by stopping the aggregation process at various times after heteroaggregation of microgel and latex particles has commenced. The addition of small silica particles is expected to reverse the surface charge of the cationic microgel particles thereby restabilizing the suspension and preventing further aggregation with the anionic latex particles. Controlling the size of the heteroaggregates is expected to enable control of the porosity

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(3) Omidian, H.; Roca, J. G.; Park, K. J. Controlled Release 2005, 102, 274.
of the aggregates, and also, potentially, to limit the viscosity of the bulk suspension by preventing the formation of large scale aggregate networks.

Heteroaggregate porosity is also strongly influenced by the extent of electrostatic interactions, which are characterized by the Debye length. In this present study, the Debye length is altered by changing the electrolyte concentration, affecting both the rate of heteroaggregation and the internal structure of heteroaggregates. The incorporation of swellable, pH-responsive microgels has several potential advantages, including improved particle contact due to the deformability of the microgels, mechanical flexibility of aggregates and reversible changes in the porosity after they have been formed, all of which expand the potential applications of the aggregates.

**Experimental Section**

**General Materials.** High purity water (resistivity 18.2 MΩ cm) supplied by a Millipore MilliQ system was used throughout. KCl solutions were prepared from analytical grade reagent (BDH, Prod. 101984L, 99.5%). Silica particles were supplied by Aldrich (Ludox AS-40, Cat. 42,084-0). All of the various particle types used in this study were dialyzed against MilliQ water using dialysis tubing with a nominal pore size of 2.5 nm (Visking) to remove impurities. Dialysis tubing was boiled in MilliQ water and autoclaved before use.

**Particle Preparation.** Anionic polystyrene latex particles were synthesized from styrene monomer (Aldrich, Cat. S4,97-2), using potassium persulfate initiator (Aldrich, Cat. 37,982-4), via free radical emulsion polymerization with an initiator (2,2′-azobis(2-methylpropionamidine) dihydrochloride, Aldrich, Cat. 44,091-4). The cationic latex returned an electrophoretic mobility of $-5.65 \times 10^{-7} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$ in 0.01 mM KCl and an average hydrodynamic diameter of 556 nm (polydispersity 0.05).

Cationic latex was prepared by the same technique using a different initiator (2,2′-azobis(2-methylpropionamidine) dihydrochloride, Aldrich, Cat. 44,091-4). The cationic latex returned an electrophoretic mobility of $+4.27 \times 10^{-8} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$ in 0.01 mM KCl and a hydrodynamic diameter of 409 nm (polydispersity 0.09).

The poly(vinylpyridine) (PVP) microgels were synthesized from 2-vinylpyridine monomer (Aldrich, Cat. 13,229-2) cross-linked with 1.5 wt % divinyl benzene (Aldrich Cat. 41,4565) by free radical emulsion polymerization with an initiator (2,2′-azobis(2-methylpropionamidine) dihydrochloride, Aldrich, Cat. 44,091-4) using a method established previously in our laboratory.

The microgels were dialyzed using the same method that was used for the latex. An electrophoretic mobility of $+3.15 \times 10^{-8} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$ was recorded in 0.01 mM KCl at a pH of 5.5 and an average hydrodynamic diameter of 454 nm (polydispersity 0.06) was measured. The type of microgel has previously been shown to swell under acidic conditions (pH < 4.5); however, in this present work, the microgels were characterized and used in their shrunk state within the pH range of 5.5–7. Measurements of 76 microgel particle diameters obtained from SEM images returned an average diameter of 388 nm, suggesting some shrinkage of the microgel occurs due to loss of water during the drying process.

**Preparation of the Porous Heteroaggregates.** The standard procedure for preparing porous heteroaggregate samples was as follows. With the exception of sample G (Table 1), separate suspensions of microgel (200 mL, 0.034 wt %), latex (200 mL, 0.098 wt %), and silica (200 mL, 0.041 wt %) were prepared at the same KCl concentration. The standard KCl concentration was 0.01 mM and the standard arrest time was 120 s (sample A and B). In sample G, the high KCl concentration (10 mM) was found to cause homoaggregation of the microgel suspension prior to mixing; therefore, no KCl was added to the microgel suspension, whereas the whole concentration (20 mM) was prepared in the anionic latex suspension.

In the first stage of mixing, the latex and microgel suspensions were rapidly combined in a 1 L glass bottle. The suspensions were not mechanically mixed during the subsequent aggregation stage, apart from two gentle inversions to redistribute aggregates halfway through the prescribed aggregation time. After a predetermined aggregation time, the silica suspension was added to stop the aggregation. The resulting suspension was then vacuum filtered. During the final stages of filtering a large quantity (>500 mL) of MilliQ water was used to rinse through any free silica particles that remained unattached to the aggregates. Immediately after filtration was completed, the filter cake was removed with a spatula and transferred to a small metal dish for freeze-drying. Great care was taken to keep the sample saturated with water before it was frozen. After immersion in liquid-nitrogen slush, the sample was rapidly transferred to the pre-cooled stage of the freeze-dryer to undergo staged heating from −60 to +25 °C over five and a half hours in a controlled pressure and temperature environment (Emitech K750). Once the freeze-dry process had been completed, the filter cakes were oven dried at 70 °C for an hour prior to measurement of the porosity.

**Mercury Porosimetry.** Mercury porosimetry was performed using a Quantachrome Autoscan 60 porosimeter and tripily distilled mercury. The data were analyzed using Quantachrome’s PoreMaster software (version 3.01) assuming advancing and receding mercury contact angles of 140°. Intrusion and extrusion of mercury up to 380 MPa was performed over a half hour period. Pressure rise was restricted to a rate of 2 MPa per minute up to 20 MPa to reduce “kinetic hysteresis” in the critical pore size region of the samples. Assuming a mercury contact angle of 140° and spherical pores, the mercury pressure can be converted into

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graphic Reference</th>
<th>[KCl] (mM)</th>
<th>Aggregation time before silica addition (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>●</td>
<td>0.01</td>
<td>120</td>
</tr>
<tr>
<td>B</td>
<td>♦</td>
<td>0.01</td>
<td>120</td>
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<tr>
<td>C</td>
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<td>0.01</td>
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<td>F</td>
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microgel particles to covered microgels. Similar charge reversals have been gates can result in the formation of high-viscosity fluids18 (using conditions for sample A in Table 1) confirmed a phoretic measurements of microgel and silica mixtures hence preventing further aggregation. Separate electro-

particles, making all of the particles species anionic and effectively reversed the surface potential of the microgel anionic latex particles. Attachment of the silica particles, which is clearly demonstrated in Figure 1, panels a and b. No anionic silica particles were found attached to the cationic microgel particles, (25) Vincent, B.; Jafelicci, M.; Luckham, P. F.; Tadros, T. F. J. Chem. Soc., Faraday I 1980, 76, 674.

selectively attached to the cationic microgel particles, which is clearly demonstrated in Figure 1, panels a and b. No anionic silica particles were found attached to the anionic latex particles. Attachment of the silica particles effectively reversed the surface potential of the microgel particles, making all of the particles species anionic and hence preventing further aggregation. Separate electrophoretic measurements of microgel and silica mixtures (using conditions for sample A in Table 1) confirmed a charge reversal from $+3.15 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$ for bare microgel particles to $-2.08 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$ for silica-covered microgels. Similar charge reversals have been reported in the literature for heteroaggregation of oppositely charged latex suspensions.25 The concentration of silica used in this study was estimated to be 15 times greater than that required for monolayer coverage of the microgel particles. SEM images in Figure 1 suggest saturation surface coverage of the microgels has been achieved under these conditions.

The sample compositions and the corresponding aggregation conditions are summarized in Table 1. Examples of linear chains, observed in all samples, can be seen in Figure 1, panel b. Linear chains, which result in relatively open aggregate structures, have also been observed in similar heteroaggregation studies by Kim et al.10 The self-assembly of the oppositely charged latex and microgel particles is a consequence of electrostatic attraction; the adoption of a chainlike structure maximizes the separation of similarly charged particles within an aggregate.

The TEM image in Figure 1, panel c, demonstrates the deformability of the microgel particles. Similar deformability has also been observed with other microgels.26,27 Identified by the presence of small adsorbed silica, the microgel particles have deformed significantly where they are in contact with the hard, spherical latex. Such deformation greatly enhances the contact area between the oppositely charged particles thereby resulting in aggregates with much greater mechanical strength than those formed from mixing hard spheres. As stated previously, the purpose of silica addition was to arrest the growth of aggregates. Using this technique, aggregates of different size can be grown as demonstrated in Figure 2. Given the aggregates are porous and their shape is nonspherical (see Figure 2, panel b), the apparent hydrodynamic diameters represented in Figure 2, panel a, will be significantly less than the outer dimensions of the aggregate; nevertheless, the data demonstrates two important points. First, considering the size measurements were made 2 h after the addition of silica particles,
a much longer time than the aggregation time prior to silica particle addition (<2 min), the presence of a clear trend in aggregate size with aggregation time indicates the silica particles have effectively stopped the growth of the aggregates. If addition of silica particles had not stopped the aggregation process, the aggregates would all grow to approximately the same size, as they would have experienced approximately the same aggregation time (i.e., 120–122 min).

Second, the trend of aggregate size with aggregation time in Figure 2, panel a, clearly shows that the aggregates increase in size with time as predicted. Inclusion of the average diameter of the primary particles in Figure 2, panel a, demonstrates that the trend qualitatively extrapolates to these initial conditions, further enhancing the confidence in this trend of aggregate size with aggregation time. The ability to qualitatively extrapolate the data in Figure 2, panel a, also implies the addition of silica particles has arrested the growth of the aggregates with a very short time (<5 s).

In summary, the silica addition effectively re-stabilizes the suspension, preventing further aggregation, and fixing the size of the aggregates as determined by the aggregation time. Aggregates are grown in the absence of shear and large aggregates appear irregular in shape (Figure 2, panel b). This has implications for packing efficiency, which will be discussed later.

**Mercury Porosimetry.** Typical examples of intruded volume as a function of mercury pressure are provided in a much longer time than the aggregation time prior to silica particle addition (<2 min), the presence of a clear trend in aggregate size with aggregation time indicates the silica particles have effectively stopped the growth of the aggregates. If addition of silica particles had not stopped the aggregation process, the aggregates would all grow to approximately the same size, as they would have experienced approximately the same aggregation time (i.e., 120–122 min).

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**Mercury Porosimetry.** Typical examples of intruded volume as a function of mercury pressure are provided in

**Figure 2.** Examples of increasing latex/microgel/silica heteroaggregate size with increasing aggregation time. In panel a the average hydrodynamic diameter is plotted versus aggregation time using the standard solution conditions. Note that the circled data point is an average of measurements for separate microgel and latex suspensions prior to aggregation, and the solid line is provided to guide the eye. Measurements relating to panel a were made 2 h after silica particle addition. In panel b, photographic evidence of aggregate size is presented for the much longer aggregation times of 1, 2, and 4 h performed with suspensions at half the standard particle concentrations. Measurements relating to panel b were made 24 h after silica particle addition. A negative image is presented to enhance the aggregate visibility.

**Figure 3.** Typical examples of mercury intrusion/extrusion volume versus pressure. Solid lines denote intrusion data, and the dashed line indicates extrusion data. The vertical line denotes an equivalent pore size of 500 nm.

**Figure 4.** Complete pore size distribution for all data sets listed in Table 1. The vertical line denotes a transition in the data at a pore size of 500 nm. Symbols are defined as "graphic references" in Table 1.

Figure 3. A number of observations can be made. First there is a large difference in the total intruded volume of mercury between the samples. In particular, although the aggregates in samples A and D are grown under the same conditions, the comparison between freeze-drying and air-drying is dramatic. The air-dried sample D has lower porosity at high pressure (small pores) and very much lower porosity at low pressure (large pores). In the air-dried sample, capillary forces have caused the structure to collapse during drying. This highlights the need for freeze-drying to maximize the porosity.

Second, the extrusion data in Figure 3 (sample A) exhibits significant hysteresis. This is common in extrusion data and in the case of an interconnected pore network is most likely the result of mercury pockets remaining trapped within "ink bottle" shaped pores. The extraction of mercury in Figure 3 sample A is clearly incomplete, thereby providing further evidence of trapped mercury. A third feature of Figure 3 is the increase in gradient that occurs between 3 and 10 MPa for samples A, J, G, and D; this transition is most easily explained by reference to a corresponding transition in the pore size distribution (Figure 4) at 500 nm. Figure 4 demonstrates that, for all samples, a clear peak in the pore volume distribution occurs between 100 and 500 nm (15 and 3 MPa), whereas
above a transition pore size of 500 nm (corresponding to 3 MPa), no sharp peaks occur. An SEM image of sample A (Figure 5) suggests the peaks in the pore size distribution below 500 nm correspond to the qualitatively uniform spacing within discrete aggregates. Conversely, the porosity above a pore size of 500 nm corresponds to voids between discrete aggregates within the filter cake.

At low pressures corresponding to large pore sizes (>500 nm), compaction of the filter cake may occur as the space between discrete aggregates is reduced. This decrease in interaggregate volume may be described by a buckling mechanism which has been proposed for low-density xerogels since mercury porosimetry of the xerogel samples in this study yielded very similar changes in gradient to those observed in Figure 3. Referring again to Figure 4, samples C and F exhibit the largest volume of porosity above 500 nm. Further analysis of all samples reveals that the proportion of volume in pores above 500 nm generally increases with the total pore volume (Figure 6). A buckling mechanism could potentially explain the trend in Figure 6, since the aggregates within more porous structures would be packed with lower efficiency due their fractal nature and could therefore be subject to a greater degree of compaction. In addition, aggregate protrusions which may break during compaction, would weaken as porosity increased and interparticle contacts were reduced.

In this present study, control of porosity is attempted through changes in porosity within discrete aggregates. Considering this and the fact there is very little volume (≤0.15 cm$^3$ g$^{-1}$) in pores below 100 nm, the remainder of this work focuses on the pores between 100 and 500 nm in diameter, which correspond to the sharp peaks observed in Figure 4 and the qualitatively uniform pore sizes in Figure 5.

With reference to Figure 7, there are a number of important comparisons to make between the different data sets. First, comparing samples A and B establishes the basic reproducibility of the data. These samples were prepared with the same procedure but on different days and were characterized separately. Second, the effect of air-drying a sample prepared under otherwise identical conditions is observed by comparing sample A to sample D. The pore volume and pore sizes have been reduced significantly in sample D and were the lowest of all of the samples. Capillary forces have led to significant compaction of the filter cake on drying; the peak in the pore size distribution is below 200 nm, and there is negligible porosity above 500 nm. These forces are much less significant for the other samples, which were all freeze-dried.

There was some concern that hydrodynamic flow during the filtration process would cause compression of aggregates. To test this hypothesis, a large aggregate (approximately 1 cm diameter), formed under the same conditions as sample A, was carefully skimmed out of the suspension before filtration. This sample is designated sample C. Significantly, although the width of the pore size distribution in sample C is less than in sample A, the maximum of the peaks occurs at very similar pore sizes (approximately 320 nm). This suggests that a large proportion of the porosity in sample A consists of porosity contained within discrete aggregates. The comparative broadening of the peak in sample A is most likely due to packing effects as a range of aggregates with different sizes are brought into contact within the filter cake. Because the peak maxima of samples A and C are nearly coincident, it would suggest that filtration has not caused significant compression of the aggregates. A recent study on the filtration of soft colloids supports this finding: in that work, 90% of the liquid pressure drop was found to occur in a small region close to the filter medium.


In an attempt to determine the highest porosity possible with the current particle system, sample F was prepared with an extended aggregation time and very low electrolyte concentration. A comparison of samples C and F in Figure 7 reveals that the pore size distributions are nearly identical. This indicates two points: that the electrolyte concentration of 0.01 mM effectively represents the lower limit for maximizing pore sizes and that the structure of sample F approaches that of a single, discrete aggregate. This second point was supported by the observation that the aggregates had formed a single gelatinous mass when transferred for filtration.

Finally, in relation to Figure 7, in sample E the cationic microgel particles have been substituted by cationic latex particles of higher charge density. The pore size and volume of sample E are significantly less than for sample A. During the growth of the aggregates, it would be reasonable to expect that aggregates within sample E would be more porous than in sample A due to the higher charge of the cationic latex and the consequent enhancement of the electrostatic interactions. However, the pore size distribution reveals the opposite, suggesting that some collapse of sample E has occurred during filtration. The latex particles are less deformable than the microgel particles, so each interparticle contact has a smaller area in sample E. Therefore, the energy barrier to structural rearrangement (e.g., by rolling) is less, and consequently, the porosity within latex—latex heteroaggregates is decreases, eq 2 predicts increasing porosity of the aggregates.

According to Bushell et al.\textsuperscript{8} the porosity $\epsilon$ is related to the fractal dimension $D_f$ through the following formula:

$$\epsilon = k_x \left( \frac{R_x}{r_0} \right)^{D_f-3}$$

where $r_0$ is the primary particle radius, $R_x$ is some measure of fractal radius, and $k_x$ is a scaling factor appropriate to method $x$. The majority of porosity measurements determined in this study relate to a filter cake consisting of many individual aggregates in close proximity. The bulk porosity of the filter cake is therefore a composite of porosity present within aggregates and between aggregates (except for sample C, which consists of a single aggregate mass), and so eq 2 cannot be applied directly to the porosity measurements within this study since the porosity term $\epsilon$ only relates to pores within aggregates. Nevertheless, eq 2 does assist in a qualitative explanation of the effect of electrolyte concentration on porosity. Previous heteroaggregation studies\textsuperscript{30} with similar particles have shown that decreasing the electrolyte concentration decreases the fractal dimension $D_f$ in the range 1.7–1.4. Assuming a similar decrease in $D_f$ occurs for samples A, G, H, and I as the electrolyte concentration decreases, eq 2 predicts increasing porosity of the aggregates. Qualitatively, this describes the trends observed in Figure 9.

It was noted previously that, during the preparation of sample G, homoaggregation of the microgel was caused by a KCl concentration of 10 mM. During the homoaggregation of sample G, the parameter $\kappa a$ (kappa $\times$ particle radius), which characterizes the range of electrostatic forces, was greater than 140. In a study of homoaggregation by Puteras et al.\textsuperscript{30} the fractal dimensions of aggregates formed under homoaggregation and heteroaggregation converge when $\kappa a$ is greater than 100. This may explain why any homoaggregation that occurred during the formation of sample G has had little effect on the trends expressed in Figure 9, since the fractal dimension, and hence porosity, of samples formed by homoaggregation or heteroaggregation would be similar.

With regard to the width of the pore size distributions, it is interesting to compare the results of Figure 8 with those of Tang et al., who used heteroaggregation of alumina and latex colloidal particles to produce macroporous materials.\textsuperscript{16} Mercury porosimetry of the samples in this study\textsuperscript{16} produced a peak in pore size distribution between approximately 200 and 400 nm, which coincides very closely to sample A in Figure 8. For sample H in Figure 8, the width of the peak in pore size is approximately halved to 100 nm, yielding a very uniform pore size and a possible advantage over samples produced by Tang et al.\textsuperscript{16}

Effect of Increasing Aggregation Time. The pore size distributions shown in Figure 10 relate to a series of samples in which the aggregation time prior to silica addition was varied from 15 to 120 s while all other parameters remained constant. Generally, there is a decrease in porosity and pore size (Figure 11), as the aggregation time decreases. In addition, there are secondary peaks present at higher pore sizes for the shorter aggregation times of 15, 45, and 90 s. These features can be explained qualitatively by referring to the theory of fractal growth introduced previously. With reference to eq 2, it can be seen that given a fixed fractal dimension, aggregate porosity increases as aggregates grow in size, a trend supported by calculations of packing density at constant fractal dimension produced by Tang.\textsuperscript{7} The precise control of total porosity by varying the aggregation time is clearly evident in Figure 11.

Conclusion

The heteroaggregation of oppositely charged latex and microgel particles provides a simple method to achieve structures of controllable porosity. The use of an excess of charged silica particles effectively stops the aggregation process, allowing a range of aggregate sizes to be prepared. The silica also provides an effective labeling mechanism that helps identify particle types of similar size by electron microscopy. By controlling the aggregation time and electrolyte concentration, precise control of the total porosity and distribution of pore sizes can be achieved. The use of soft and deformable microgel particles results in aggregates with higher porosity than those containing only hard particles.

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