

The Role of Polymer Polydispersity in Phase Separation and Gelation in Colloid–Polymer Mixtures

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Mixtures of nonadsorbing polymer and colloidal particles exhibit a range of different morphologies depending on the particle and polymer concentrations and their relative size ratios. These can be very important for technological applications, where gelation can produce a weak solidlike structure that can help reduce phase separation, extending product shelf life. However, industrial products are typically formulated with polydisperse polymers, and the consequences of this on the phase behavior of the mixture are not known. We investigate the role of polymer polydispersity and show that a small amount of larger polymer in a distribution of nominally much smaller polymer can drastically modify the behavior. It can induce formation of a solidlike gel structure, abetted by the small polymer, but still allow further evolution of the phase separation process, as is seen with a monodisperse distribution of larger polymer. This coarsening ultimately leads to gravitational collapse. We describe the full phase behavior for polydisperse polymer mixtures and account for the origin of the behavior through measurements of the structure and dynamics and by comparing to the behavior with monodisperse polymers.

Introduction

Addition of nonadsorbing polymer to a colloidal suspension induces a very rich range of microstructures, whose nature depends on the particle and polymer concentrations and the relative size of the particles and polymer.^{1,2} The addition of the polymer leads to a depletion attraction that is capable of inducing a fluid–solid transition, resulting from the formation of a gel, a connected network that spans the space and can support weak stresses. Such gels are extensively used in commercial applications such as personal care or food products, to help stabilize the system against sedimentation, thereby precluding phase separation, and increasing product shelf life.^{3–5} The nature of the fluid–solid transition depends on the range of the depletion attraction, which, in turn, depends on the ratio of the size of the polymer to the colloidal particle. For short-range interactions, gelation is induced by spinodal decomposition;⁶ the system undergoes a gas–liquid phase separation which is interrupted by the dynamical arrest of the particles in the colloid-rich region, leading to formation of the gel. By contrast, for larger ranges of the attraction, phase separation can proceed to completion, without

being interrupted by dynamic arrest leading to gelation.^{7,8} However, in the presence of gravitational effects the structure may no longer be capable of sustaining its own weight; instead, it collapses, disrupting the phase separation process⁸ or rupturing the gel that was previously formed.^{9–11} This is an undesirable effect technologically, as it can dramatically shorten the shelf life of a commercial product. This suggests that the use of shorter polymers at sufficiently high concentration is most likely of greatest practical use. However, technological polymers are very rarely monodisperse, and thus the microstructures and their behavior may be drastically modified. However, despite the practical importance, the gravitational behavior of colloid–polymer mixtures using polydisperse polymers has never been investigated.

In this paper, we investigate in detail the behavior of model colloidal particles mixed with nonadsorbing polymer with a polydisperse size distribution, similar to that often found in commercial samples. We use a predominantly short-range interaction to induce gelation. However, we show that the presence of a small concentration of much larger polymers can have dramatic consequences on the behavior. We find that only those mixtures in the proximity of the liquid–gel boundary collapse under the influence of gravitational effects. Interestingly, however, we find that the gravitational stress imposed on the network is not the ultimate cause for this behavior. Instead, it results from coarsening of the particle network due to spinodal decomposition, which results from the long-range attraction induced by the fraction of the polymer distribution with long chain lengths. We verify this by

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comparison to the behavior of a monodisperse polymer mixture for the same range of attraction, where the coarsening of the structure disappears.

Experimental System and Methods

We use an aqueous dispersion of polystyrene particles with a density $\rho = 1.057 \text{ g/cm}^3$ and an average radius $a = 1.5 \mu\text{m}$, as determined by dynamic light scattering.^{12,13} We use polyethyleneglycol (PEG) (American Polymer Standard Co.) with an average molecular weight $M_w = 475\,500 \text{ g/mol}$, polydispersity index $M_w/M_n = 2.63$, and mean radius of gyration $\bar{r}_g = 40 \text{ nm}$, which we estimate from the average molecular weight.¹⁴ Here, M_w and M_n are the mass- and number-averaged molecular weights, respectively. We also add a 1:1 salt, NaClO_4 , at 5 mM to reduce electrostatic interactions. We homogenize the samples by tumbling for 24 h.

Results and Discussion

The rate of sedimentation of the colloidal particles is dependent on the microstructure of the colloid–polymer mixture. Sedimentation is driven by the density mismatch between the solvent and the colloidal particles, $\Delta\rho$, that results in a body force on the individual particles, $F = \frac{4}{3}\pi\Delta\rho ga^3$. For a particle suspension, the settling rate is hindered by solvent backflow.⁴

However, settling in particle gels is more complicated as the gravitational forces act on and are transmitted through the entire network, resulting in a distinctive settling behavior. By monitoring the time-dependent height profile of the sample as it sediments, it is possible to distinguish between the two cases.

At low polymer concentration, the depletion-induced attraction between particles is small and the interface immediately begins to fall, with a constant rate, $v = (1.5 \pm 0.2) \cdot 10^{-7} \text{ m/s}$, as shown in Figure 1 for a polymer concentration $c_p = 1 \text{ mg/mL}$ and a particle volume fraction $\phi = 0.1$ (closed squares); this value is consistent with hindered settling models for dispersed particles,¹⁵ where

$$v = \frac{2\Delta\rho ga^2}{9\eta}(1-\phi)^{5.5} = 1.8 \times 10^{-7} \text{ m/s}$$

with η the viscosity of the solution. At high polymer concentration, the attraction between particles is large. As a result, the height of the interface evolves in a different fashion, as shown in Figure 1 for $c_p = 20 \text{ mg/mL}$ at the same ϕ (closed triangles). The height evolution in this case quantitatively agrees with poroelastic models for the gravitational compression of particle gels.^{16–18} In this case, the height evolution of the interface is determined by the balance of the gravitational and elastic stresses imposed on the network, and by the viscous stress due to solvent backflow through the network as it is compressed.

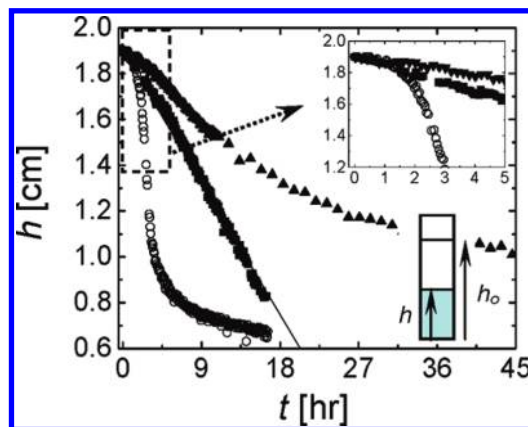


Figure 1. Experimental height profiles at different polymer concentrations: (■) $c_p = 1 \text{ mg/mL}$, (○) $c_p = 7.5 \text{ mg/mL}$, and (▲) $c_p = 20 \text{ mg/mL}$. We measure the height from the bottom of the cell, as shown in the schematic, where $h_0 = (1.90 \pm 0.05) \text{ cm}$ is the initial height. (Upper inset) Expanded details of the initial evolution for a time window of 5 h.

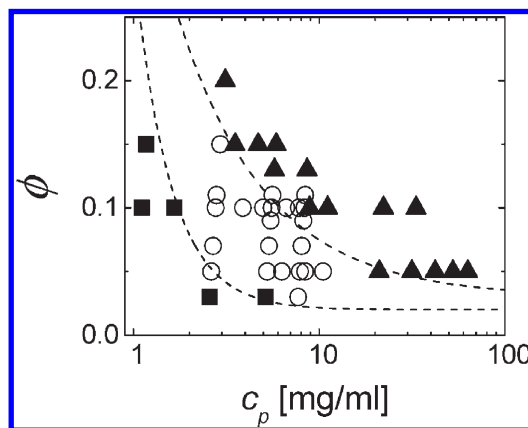


Figure 2. Diagram for the behavior of mixtures of polystyrene colloidal particles and polyethylene glycol polymer as a function of the particle volume fraction ϕ and the polymer concentration c_p : (■) sedimentation; (○) collapse; (▲) compression.

Surprisingly, at intermediate polymer concentrations, there is a fundamentally different behavior. Initially, the interface slowly moves but, after some time, abruptly and rapidly falls, as shown in Figure 1 for $\phi = 0.1$ and $c_p = 7.5 \text{ mg/mL}$ (open circles),¹⁹ a behavior which is similar to transient gelation,^{9–11} where a gel forms and subsequently collapses under the influence of gravitational stresses.

Using the temporal evolution of the interface as a criterion, we summarize the behavior of our colloid/polymer system in a ϕ – c_p diagram, shown in Figure 2. For low ϕ or low c_p , the system undergoes hindered sedimentation (closed squares), consistent with the absence of gelation. By contrast, at high ϕ or high c_p , the system exhibits a compression behavior (closed triangles) indicating the presence of a particle gel. Between these two behaviors, for intermediate ϕ and intermediate c_p , we find a region in the ϕ – c_p diagram corresponding to a behavior which is reminiscent of transient gelation (open circles).

Interestingly, this transient behavior is linked to a coarsening of the structure, as shown in Supporting Information, Movie S2, for $c_p = 5 \text{ mg/mL}$. This coarsening, which is reminiscent of “curdling”, precedes the collapse of the structure. Thus, although collapse must result from gravitational stress, it is unclear whether this external stress is the ultimate cause of the collapse, or whether

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(19) The interface evolution for all observed behaviors is shown in Movie S1 of the Supporting Information: (a) $c_p = 1 \text{ mg/mL}$, (b) $c_p = 2.5 \text{ mg/mL}$, (c) $c_p = 5 \text{ mg/mL}$, (d) $c_p = 7.5 \text{ mg/mL}$, (e) $c_p = 1 \text{ mg/mL}$, (f) $c_p = 2 \text{ mg/mL}$, (g) $c_p = 3 \text{ mg/mL}$. Sample a sediments downwards, samples b–d show coarsening of the structure followed by collapse, and samples e–g show gel compression. For all samples $\phi = 0.1$.

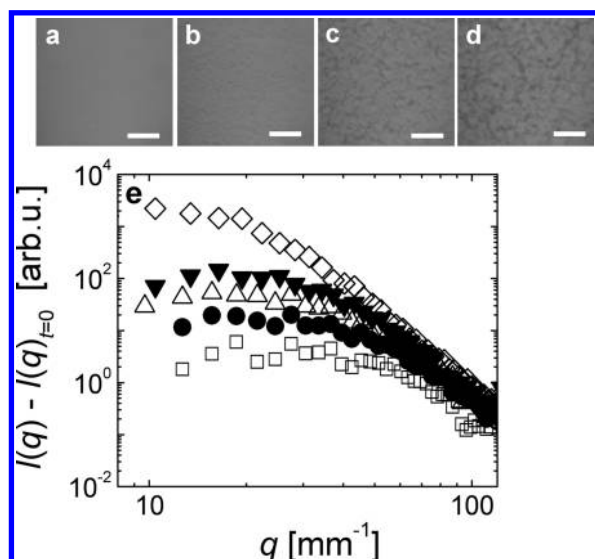


Figure 3. (a–d) Images of the coarsening process for $\phi = 0.1$ and $c_p = 5$ mg/mL, at different times: (a) $t = 0$; (b) $t = 300$ min; (c) $t = 600$ min; (d) $t = 900$ min. The scale bar corresponds to $300 \mu\text{m}$. (e) Azimuthally averaged Fourier transform of the images at different times: (\square) $t = 80$ min; (\bullet) $t = 170$ min; (\triangle) $t = 280$ min; (\blacktriangledown) $t = 400$ min; (\diamond) $t = 1200$ min.

the coarsening behavior that precedes the collapse is, in some way, implicated in the collapse itself. To investigate this, we prepare samples at intermediate ϕ and c_p and vary both the initial height and the density difference between the particles and the solvent, by using water/D₂O mixtures, while keeping both ϕ and c_p constant. In this way, we span 3 orders of magnitude in the magnitude of the total gravitationally induced stress at the bottom of the gel $\sigma_g = \Delta\rho g\phi h_0$, from 10^{-3} Pa to 1 Pa; this is the “weight” of the gel, which is supported at the bottom of the sample. We find that the structure of the colloid/polymer mixtures coarsens to some extent before it actually collapses due to the gravitational stress. Interestingly, the time for this coarsening to become appreciable in our images does not change with σ_g and always remains equal to ~ 15 min.

As a result, we conclude that the coarsening behavior is not dependent on the gravitational stress, thereby implying that the presence of this stress is ultimately not the mechanism responsible for the temporal evolution of our samples. To further investigate this, we prepare a density-matched sample inside a glass cuvette of height 4 cm and an optical path length of 1 mm, and follow the time evolution of the sample using a CCD camera and a high magnification objective, focused on a small region in the middle of the cuvette. We do not observe any collapse of the structure within the experimental time-window since σ_g is so small. However, as time proceeds, the system separates into colloid-poor and colloid-rich regions, as shown in the optical images of Figure 3 and in Supporting Information, Movie S3, where darker regions correspond to colloid-poor regions and brighter regions correspond to colloid-rich regions.

The development and growth of these domains are reminiscent of spinodal decomposition.^{7,8,20–22} To elucidate this, we calculate the modulus of the 2-D Fourier transform (FT) of the images recorded on the CCD and subtract the corresponding result for the first image, at $t = 0$, which we use as background. Since the

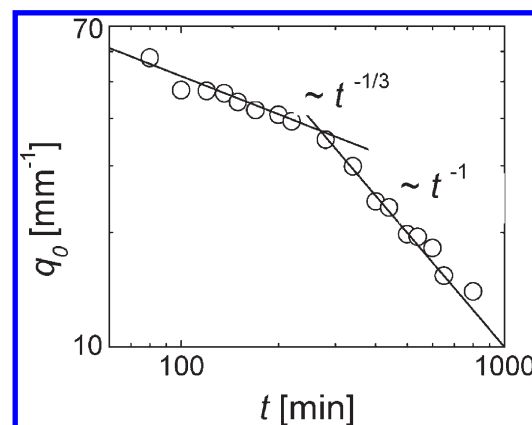


Figure 4. Time dependence of q_0 exhibiting a clear crossover from early to late stage dynamics.

particles are small on the scale of the image, we can ignore their form factor, which is essentially constant over the image; thus we do not normalize by the form factor. In addition, since the sample is isotropic at all times, we perform an azimuthal average of the final result, which we plot as a function of the wave vector, $q = 2\pi/r$, with r being the distance from the center of the image, in Figure 3e. The resultant intensity profiles are characterized by a plateau region at low q and a crossover to a time-independent decay at high q . Both the height of the plateau and the crossover vary with time; the height of the plateau increases, while the position of the crossover shifts to lower q . This result suggests that there is a characteristic length scale growing with time as coarsening proceeds.

To quantify this growth, we determine the crossover, q_0 , by identifying the intersection of two straight lines corresponding to the flat and decaying parts of the curves, and plot its time evolution in Figure 4. At short times, $q_0 \approx t^{-1/3}$, while for $t > 266$ min, $q_0 \approx t^{-1}$. This scaling behavior agrees with that expected for spinodal decomposition,²³ where the short-time behavior is governed by diffusion and the long-time behavior is driven by a competition between interfacial and viscous forces associated to the growth. In our experiments, the crossover between these two regimes occurs for $q_c \approx 37 \text{ mm}^{-1}$ and $t_c \approx 266$ min.

For systems undergoing spinodal decomposition, the crossover from the early to the late stage is expected to occur when $q_c \xi \approx 0.1$ ²³ and $t_c/\tau \approx 300$ ⁷, where

$$\tau = \frac{6\pi\eta\xi^3}{k_b T}$$

is the relaxation time of a fluctuation with wave vector $1/\xi$.²⁴ Using our experimental results for q_c and t_c , we find $\xi \approx 2.7 \mu\text{m} \approx 2a$ and $t_c/\tau \approx 198$, which are both in excellent agreement with theoretical expectations and with values recently reported for colloid–polymer mixtures in microgravity.⁷

This suggests that the coarsening behavior, even when the densities of the colloids and solvent are not matched, is due to spinodal decomposition. However, if the densities are not matched, spinodal decomposition is interrupted by the presence of gravitational stresses. We therefore propose that the nonadsorbing polymer induces the requisite attraction to initiate spinodal decomposition of the mixtures. The initially homogeneous mixture then evolves into a bicontinuous network of colloid-poor

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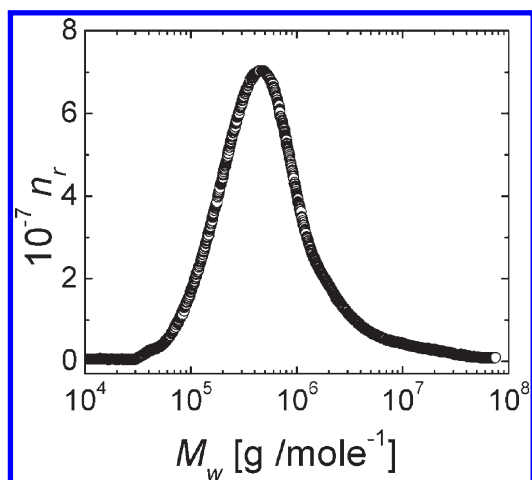


Figure 5. Molecular weight distribution of the polydisperse polymer in terms of the chain number normalized by the total number of chains, n_r , and the molecular weight, M_w .

and colloid-rich domains. The structure continues to coarsen and eventually loses mechanical strength; it fractures and collapses under the presence of the gravitational stress.

Surprisingly, however, the typical range of the attractive interaction in our experiments is

$$\zeta = \frac{\bar{r}_g}{a} \approx 0.03$$

which is much lower than those that are typically required to induce phase separation. However, this value is based on the average molecular weight of the polymer, M_w ; because of the polydispersity of the polymer, there is a sizable fraction of chains which are several orders of magnitude larger than the mean, as shown in Figure 5.²⁵ Despite the relatively smaller concentration of these larger chains, we hypothesize that they nevertheless determine both the magnitude and width of the attraction, resulting in a weaker and wider attraction than would be expected from the peak of the M_w distribution, and causing the mixtures to exhibit a transient gel behavior.

To test this hypothesis, we perform the same experiments with monodisperse polymer. Mixtures were prepared with the same colloidal particles but using a PEG (American Polymer Standard Company, Mentor, OH) of $M_w = 438\,000$ g/mol, but with a much smaller polydispersity index, $M_w/M_n = 1.18$. In these mixtures, the coarsening behavior is not observed. Instead, we observe only hindered sedimentation at low polymer concentrations and gel compression at high polymer concentrations, as shown in Figure 6 for $\phi = 0.05$ and c_p ranging from 5 mg/mL (right vial) to 60 mg/mL (left vial). The transition between these two behaviors occurs between $c_p = 20$ mg/mL and $c_p = 30$ mg/mL; for $c_p = 20$ mg/mL, the system exhibits hindered sedimentation, as shown by the squares in Figure 6b, while for $c_p = 30$ mg/mL, the system exhibits gravitational compression, as shown by the circles in Figure 6b. This behavior is in striking contrast to that observed with the polydisperse polymer, emphasizing the important role of the largest polymer chains on the gravitational stability of colloid/polymer mixtures when the polymer is polydisperse, and confirming our hypothesis that it is these larger polymer chains that determine the behavior of the mixture. However, by comparing the behavior presented in Figure 6 with that of the polydisperse

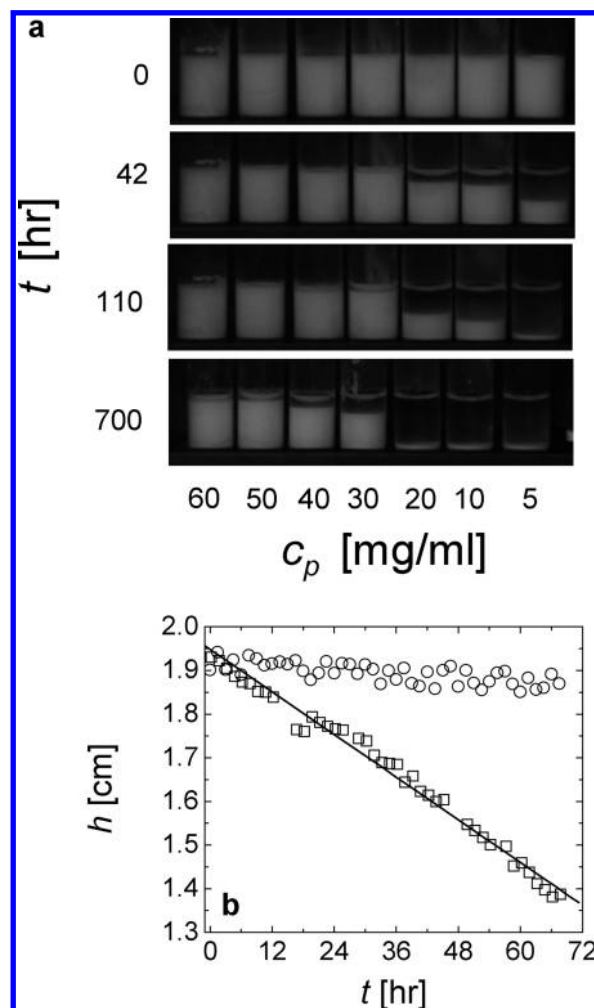


Figure 6. (a) Snapshots at different stages during the evolution of samples prepared with monodisperse polymer. The volume fraction of colloidal particles is $\phi = 0.05$ in all samples. (b) Experimental height profiles at two polymer concentrations: (\square) $c_p = 20$ mg/mL, (\circ) $c_p = 30$ mg/mL. The line represents the linear fit to the experimental points. From the slope of this fit, we obtain a velocity $v = 2.3 \times 10^{-8}$ m/s, which is in good agreement with the theoretical expectation, $v = \frac{2}{9} \frac{\Delta \rho g a^2}{\eta} (1 - \phi)^{5.5} = 1.6 \times 10^{-8}$ m/s

case (see Figure 2, for $\phi = 0.05$), we observe that also in this case a polymer concentration of $c_p \approx 20$ mg/mL marks the formation of a gel that compresses in time. Thus, at high polymer concentrations the overall behavior of the system is mainly controlled by the smaller rather than by the larger polymer chains. It is thus apparent that to properly account for the behavior of colloid–polymer mixtures prepared with polydisperse polymer, the full nature of the polymer distribution must be considered. This is of particular importance in practical applications of these mixtures.

Conclusion

We find that polymer polydispersity can play a crucial role in the phase behavior of colloid–polymer mixtures. For broad polymer size distributions, the large polymers can effectively increase the range of the depletion attraction giving rise to spinodal decomposition rather than fully dynamically arrested gelation. By contrast, for monodisperse polymer, spinodal decomposition is dynamically arrested resulting in gelation. The effect of gravitational stresses can be dramatically different depending on whether the suspension phase separates or forms a gel. While for our phase separating samples, the system exhibits

(25) The molecular size distribution is measured by gel permeation chromatography and is provided by the supplier.

a sudden collapse, for our gelling samples, only a slow compression of the gel is observed. These results demonstrate that the stability of colloidal structures formed by the inclusion of non-adsorbing polymer can depend on the details of the polymer polydispersity. This is of particular importance for applications based on colloid–polymer mixtures, where not only the colloidal suspension but also the polymer can be polydisperse. In particular, these results are important for commercial products, where the coarsening and collapse behavior can severely limit the shelf life and utility of the final product.

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Supporting Information Available: Movie S1: Evolution of the system at constant $\phi = 0.1$ and different polymer concentrations: (a) $c_p = 1$ mg/mL, (b) $c_p = 2.5$ mg/mL, (c) $c_p = 5$ mg/mL, (d) $c_p = 7.5$ mg/mL, (e) $c_p = 1$ mg/mL, (f) $c_p = 2$ mg/mL, (g) $c_p = 3$ mg/mL. Movie S2: Close-up evolution of the experiment with $\phi = 0.1$ and $c_p = 5$ mg/mL where the coarsening behavior can be observed. Movie S3: Time evolution of the coarsening of a density matched sample with $\phi = 0.1$ and $c_p = 5$ mg/mL. The image spans a region in the cell of 5 mm^2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.