Formation and collapse of gels of sterically stabilized colloidal particles

James R Weeks†, Jeroen S van Duijneveldt‡ and Brian Vincent

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

E-mail: `j.s.van-duijneveldt@bristol.ac.uk`

Abstract. Colloidal silica spheres (diameter 88 nm) with a thick steric stabilization layer of polystyrene (PS; $M_w = 26\,600$ g mol^{-1}) were prepared. In cyclohexane, a marginal solvent for PS, particle aggregation and gelation were observed on lowering the temperature. Near the gelation temperature and at particle concentrations of a few per cent by weight, the gels were sufficiently weak to slowly compact under gravity. On quenching to slightly lower temperatures, the gels still settled, but the top of the sediment did not become flat, as is usually the case. This seems to be related to an unusual mechanism for gel compaction, which starts by forming a more dense structure at the top of the sample. It is proposed that this is related to the entangled polymer chains on neighbouring particles resisting substantial rearrangement of the local structure. The transient gelation phenomenon, observed previously for mixtures of colloid and non-adsorbing polymer, has so far not been observed for our system.

1. Introduction

A suspension of colloidal particles can form a gel, consisting of a percolating particle network, when the particle concentration and strength of attraction between particles are sufficiently high. When weak gels are produced, they may undergo slow settling under gravity. Such gels are of great practical importance, for instance for foods, pharmaceutical and agrochemical formulations, and paints. The settling behaviour is an important property, as it may determine the shelf-life of a product. There is also significant interest in colloidal suspensions as 'model liquids', on which to test theories of the liquid state. For a recent review of aggregation and gelation in model colloids, see reference [1].

Here we study particles that are stabilized in a non-aqueous solvent by a grafted polymer layer. At high polymer grafting density, and in a good solvent for the polymer, a stable suspension may thus be obtained [2]. When the solvent quality is lowered, however, the steric stabilization tends to fail, typically near the theta temperature for the polymer. Model systems with thin stabilizing layers have already been studied in detail (see, for instance, reference [3], and references therein). In this work, however, particles with a relatively thick stabilizing layer are used. The suspensions are made to gel by lowering the temperature.

A number of studies have been devoted recently to the phenomenon of 'transient gelation', where particle gels are formed that undergo a sudden transition from a slow initial settling regime to a rapid second regime [4–7]. Motivated by this work, we have investigated the

---

† Present address: ChemWeb Incorporated, 84 Theobald's Road, London WC1X 8RR, UK.
‡ Author to whom any correspondence should be addressed.

settling behaviour of the gels formed in our model system. In a few cases, the behaviour appears to be qualitatively different from previous observations, whereas transient gelation has not (yet) been observed.

2. Experimental procedure

2.1. Particle preparation

Monodisperse silica particles were prepared following the procedure initially developed by Stöber *et al* [8]. In this reaction, tetraethylorthosilicate (99%, Aldrich) is hydrolysed at room temperature in an ethanol (99.9%, Haymet Limited)/water solution, using ammonia (66% aq., Fisher) as a catalyst. Deionized water was obtained using a Millipore Milli-Q purification system. The size of the particles produced in the hydrolysis was set by the relative concentrations of the reagents, as described by Bogush *et al* [9]. Photon correlation spectroscopy (PCS) was used to determine the final particle size. The bare particle diameter was 88 nm. Transmission electron microscopy gave a particle diameter of 74 nm, with a relative polydispersity of 0.10.

Following the work of Edwards *et al* [10], polystyrene (PS) chains were prepared by anionic polymerization of styrene (99%, Aldrich) using sec-butyl lithium (1.3 M, Aldrich) as initiator and toluene (99.8%, Aldrich) as the solvent. The chains were terminated with a reactive end-group for grafting to the silica surface. Methyltrichlorosilane, followed by methanol were added to the living polymer, resulting in reactive methoxy groups. Details are given in reference [11]. The molecular weight was determined by GPC, at Rapra UK Limited, to be $26\,600$ g mol^{-1} with a polydispersity of 1.02.

The method of grafting the polystyrene chains to the silica particles is based on the work of Edwards *et al* and Vincent [10, 12]. The bare silica particles were first redispersed from ethanol into dimethylformamide (DMF, 99%, Aldrich). The polystyrene was also dissolved in the DMF/silica dispersion to high concentration, and the mixture was refluxed for several days. The particles were then transferred into toluene by repeated centrifugation/redispersal cycles. More polystyrene was dissolved and the mixture was refluxed for a further 4–5 days. The final batch of grafted particles was redispersed in fresh toluene. The surface coverage of polystyrene chains was determined by elemental analysis, resulting in a moderately high value of 2.3 mg m^{-2}, corresponding to 19 nm^2/chain.

2.2. Phase behaviour

For the subsequent experiments, the grafted particles were redispersed in cyclohexane. At 40 °C, a stable suspension resulted. The hydrodynamic diameter, determined by PCS, was 111 nm, giving a thickness of 12 nm for the grafted polymer layer. Subsequently, samples were subjected to temperature quenches, lowering temperature by a further 0.5 °C for each further experiment. After each experiment, the sample was equilibrated again at 40 °C. PCS and turbidity measurements were used to locate the highest temperature where aggregation would occur. No change of the particle diameter or sample turbidity was detected above this temperature. The aggregation behaviour of these particles will be discussed in a separate paper [13].

In this work, the particle concentration is expressed as the mass fraction, m_r, determined by drying a known amount of sample. Assuming a silica density of 1.9 g cm^{-3}, and using the hydrodynamic diameter of the grafted particles, an effective volume fraction of the particles could be calculated. At the moderate concentrations studied here, $\phi \approx 0.8 \times m_r$ [13].

For particle concentrations of at least a few per cent by weight, it was possible to produce a particle gel, by quenching to a lower temperature. The onset of gelation was detected by placing the samples in a laser beam (5 mW, 632.8 nm) and observing the speckle pattern at small scattering angles. Samples were considered to be in the gel state if the vigorous fluctuation of the speckles, due to Brownian motion, visibly arrested within 30 minutes.

The settling behaviour of the gelling samples as a function of temperature was investigated at two particle concentrations (see figure 1). Samples were prepared in flat glass cells of 2 mm path length, and quenched in a water bath. The settling behaviour was recorded using a video camera and a computer, equipped with a frame grabber. In all of the gelation and sedimentation experiments, the total sample height was approximately 30 mm, and the cell width was 10 mm.
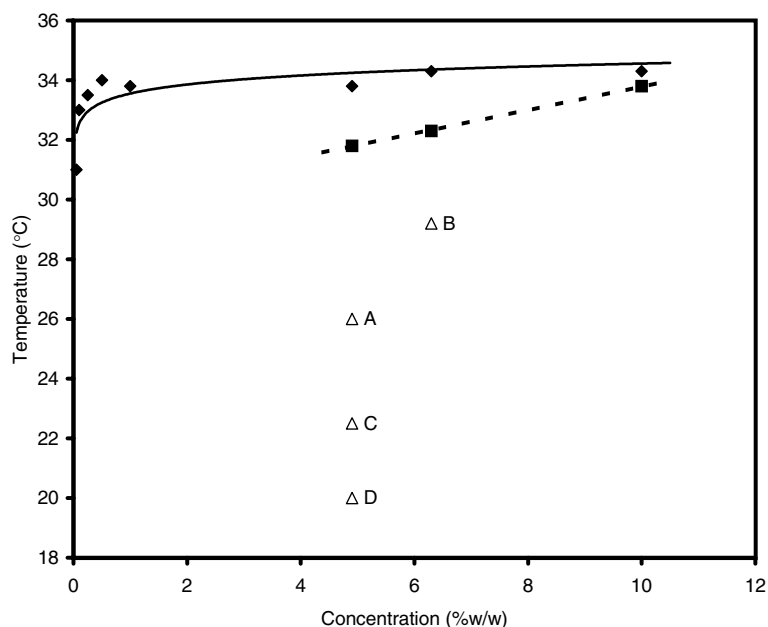

Figure 1. Phase behaviour as a function of temperature. The onset of aggregation (diamonds and solid line) and the gel line (squares and dashed line) are indicated (lines are drawn to guide the eye). The open triangles and letters denote gel collapse experiments (see the text).

3. Results

In figure 1, the phase behaviour as a function of quench temperature is summarized. The onset of particle aggregation is found at 34 °C for moderate particle concentration, and at slightly lower temperature at lower particle concentrations. Gels were only observed for samples with a concentration of at least a few per cent by weight. At lower particle concentration, aggregates would form which would subsequently settle down, but speckle arrest was not observed. The behaviour of the gelling samples, denoted by letters A–D in figure 1, will be discussed in more detail here.

Experiments A–C gave rise to weak gels, which slowly settled under gravity. Representative images are shown in figure 2†. In general, quenches to lower temperatures resulted in stronger gels, which sedimented less rapidly. In the case of sample A, the gel was found

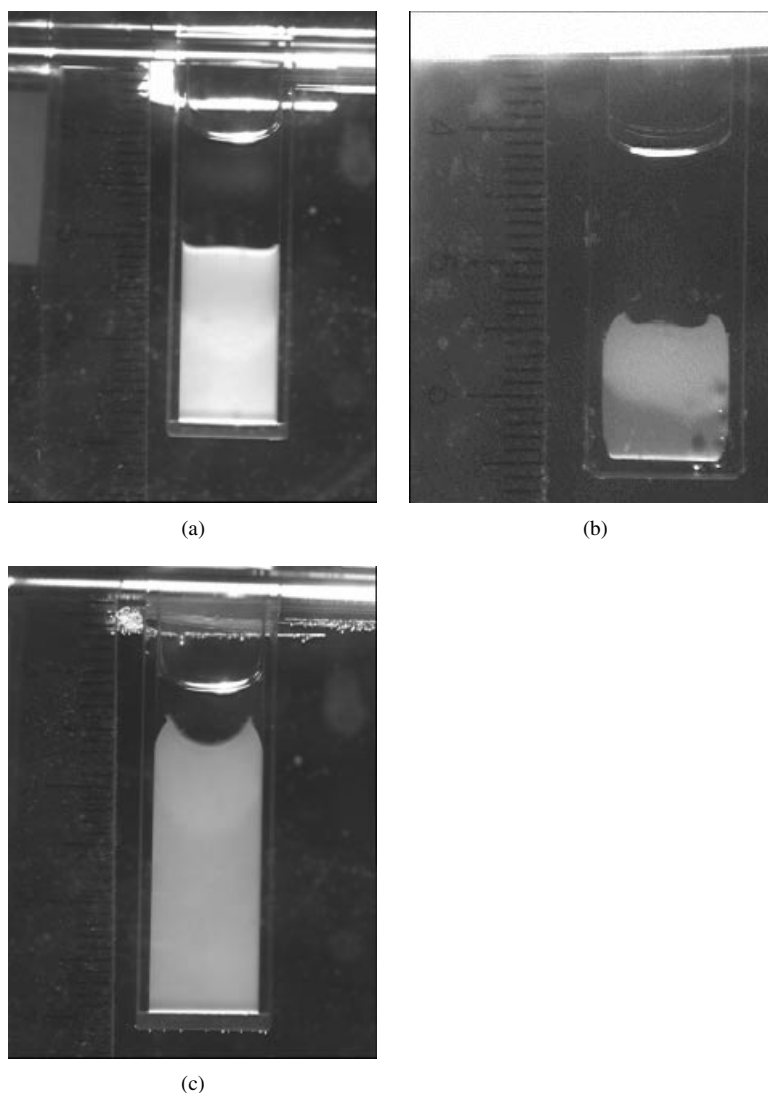† The electronic version of this paper also has animated GIF movies of the settling process.

(a)

(b)

(c)

Figure 2. Video images of collapsing gels (the scale bar is in cm). The sizes of the animated GIF movies are indicated in brackets. (a) Experiment A, final time 23 h (1.7 Mbyte); (b) experiment B, image taken after 24 h, final time 37 h (760 kbyte); (c) experiment C, final time 25 h (1.4 Mbyte).

to settle rapidly and the appearance of the gel remained homogeneous. A rather different behaviour was observed in experiment B. The top of the sediment did not become quite flat in this case, and a bright region appeared at the top of the sediment, as settling proceeded, and appeared to 'consume' the region beneath it. As we will discuss below, we believe this to be the result of this top layer of the sediment having a higher concentration than the remainder. In experiment C, the formation of a brighter top region in the sediment was also faintly visible. The top of the sediment develops a structure with two 'ears', which originate from the initial structure of the gel at the sample meniscus. The sediment shape observed previously for experiment B is similar, although the structuring is less pronounced.

It was observed that aggregation was not quite reversible—if a sample was allowed to

aggregate or gel for a prolonged period (a day for instance), it would become impossible to fully redisperse the particles after increasing temperature again. This problem was more pronounced at higher particle concentrations. Therefore, the observations of gelling samples have been limited here to timescales of about one day. In general, if a sample is left for a long time (a week or more), a final state will be reached, where the sediment is strong enough to withstand further compaction under gravity. The final sediment is taller when the initial particle concentration is higher, or temperature lower (stronger particle attractions). After sufficiently deep quenches, such as for sample D, the gel was not found to undergo settling at all after a day.

It should be noted that the settling of the gels appeared to be a steady process, with no initial latency period as observed for depletion-induced gels [5, 6].

4. Discussion

In general, the phase behaviour observed here (figure 1) is very similar to that observed previously for silica particles to which (much shorter) chains of stearyl alcohol had been grafted (see, for instance, reference [3]). On decreasing the solvent quality, by lowering the temperature, the particles aggregate; at sufficiently high concentration and low temperature, a gel state is obtained. At a particle concentration of 10% by weight, the gel transition almost coincides with the onset of aggregation, but increasingly deep quenches are needed to obtain a gel as the concentration is lowered. Below a few per cent by weight, gels were not observed. For the stearyl alcohol particles, this behaviour has been modelled using the Baxter adhesive hard-sphere interaction potential [3, 14]. For the present colloidal system, the stabilizing polymer layer has a thickness of about 12 nm. Nevertheless, it is expected that the range of attractive interactions in a poor solvent for the polymer is rather narrow, probably no more than a few nm, depending on temperature [13]. The similarities in the phase behaviour support this. A more detailed comparison of the phase diagrams will be made elsewhere [13].

Usually, a gel will settle if the gravitational stress exceeds the yield stress of the gel (see, for instance, Senis and Allain [15]). A sediment with a flat surface tends to be formed, and settling proceeds until the sediment has a sufficiently high concentration (and associated yield stress) to support its own weight. Furthermore, it is worth noting that, in the settling of such aggregated suspensions, the particle concentration is always expected to be highest at the bottom of the sample, barring any unusual settling instabilities (see, for instance, references [16, 17]. Note also that in reference [17], the sediment sometimes showed a very slight increase in density near the top—much weaker than the effect reported below). The behaviour observed in experiment A seems to fit this scenario.

A qualitatively different behaviour is observed in experiments B and C. The top of the sediment retains (some of) the initial structure, present due to the presence of the curved meniscus of the suspending liquid. Furthermore, the top region of the sediment becomes more opaque as settling progresses—we believe this to be the result of the concentration in this region being higher. To rationalize these observations, we propose the following qualitative mechanism for the gel settling in this case (see figure 3). The gel compacts mainly under the influence of inter-particle attractions, which favour a final state which is more concentrated than the initial suspensions. Gravity plays a minor role. In the bulk of the sample, the forces on a particle balance out (panel (a)). The wall also provides an opposing force (so the gel is not pulled away from the wall). The only place where motion begins is at the meniscus, where no opposing upward force is offered. Due to the curvature of the liquid meniscus, the colloid present near the walls is drawn not only down, but also towards the centre of the sample. As a result, a region of higher density is formed near the top of the sediment. After settling has
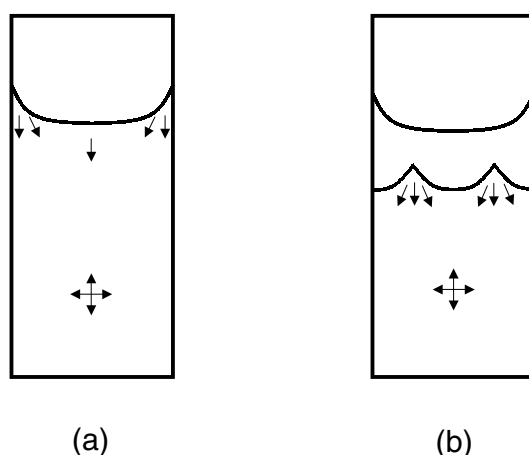
Figure 3. The proposed explanation of settling behaviour in experiments B and C (see the text). (a) The initial sample. (b) The situation after settling has proceeded and the top of the sediment has reached its final shape.

proceeded for a while (panel (b)), a 'steady state' is achieved with symmetrical 'lobes' (as in experiment C), where the top of the sediment does not change shape anymore, because the forces on the top of the sediment now only work downward.

In experiment B, the formation of the symmetrical sediment shape is not as well developed as in experiment C—possibly because the top of the sediment quickly reaches such a high concentration that no further motion is possible. As soon as the dense region has 'consumed' all the lower-density material below it, sedimentation seems to halt. The density in this final state is about 22% by weight (effective volume fraction 0.17).

In a number of previous studies, the phenomenon of transient gelation has been observed [4–7]. In these studies, a sudden increase in settling velocity has been noted after a well-defined initial delay period, during which slow settling occurs. Using dark-field observations of colloid–polymer mixtures, where attractions result form depletion of the non-adsorbing polymer between colloidal particles, the end of the delay period was found to coincide with the formation of macroscopic cracks in the sample structure [17]. For stronger attractions (higher concentration of non-adsorbing polymer), a steady settling was observed. On a microscopic level, formation of fractures was observed in similar systems [6]. For our samples, we have not observed a sudden increase of settling behaviour so far. Any such effects are likely to be found near the gelation line, if at all. Possibly entanglement of the polymer layers prevents large-scale formation of cracks.

Particles stabilized with (short) stearyl alcohol chains were also found to undergo gelation under sufficiently poor solvent conditions. For these gels, obtained with similar sized particles to those used in the present work, no settling has been reported at all, however [3]. It is not clear whether the thick polymer layers, used in the present work, are a prerequisite for the settling behaviour that we observed.

A systematic investigation of the gel behaviour as a function of temperature and concentration has so far been prevented by the limited amount of material available, and the fact that the gelation was not quite reversible. One possible reason for this irreversibility is an entanglement of the polystyrene chains on neighbouring particles—effects of this have also been noted recently in measurements of the surface force between PS layers in a good solvent [18]. Furthermore, small silica particles, grafted with poly(dimethylsiloxane) (PDMS),

and suspended in a good solvent (heptane), were found to gel irreversibly on increasing concentration. This was ascribed to a strong physisorption of PDMS chains to available surface patches on neighbouring particles [19]. These bridging effects may play a role here as well, as PS is also known to adsorb onto silica from cyclohexane [20].

Several avenues for further study of the peculiar gelation behaviour in these sterically stabilized suspensions are open, provided a sufficient supply of sample can be prepared. First of all, a closer examination of the behaviour near the gelation line might reveal a region of transient gelation behaviour. It would be of interest to employ a concentration profiling technique, using ultrasound measurements for instance, to quantify the formation of a dense region near the top of the sediment, observed here. Measuring the rheological properties would greatly assist the interpretation of the settling behaviour. Finally, microscopy and dark-field observation techniques could be used to characterize the gel break-up in more detail.

Acknowledgments

References

[1] Poon W C K and Haw M D 1997 Mesoscopic structure formation in colloidal aggregation and gelation *Adv. Colloid Interface Sci.* **73** 71–126

[2] Napper D H 1983 *Polymeric Stabilization of Colloidal Dispersions* (London: Academic)

[3] Verduin H and Dhont J K G 1995 Phase diagram of a model adhesive hard-sphere dispersion *J. Colloid Interface Sci.* **172** 425–37

[4] Allain C, Cloitre M and Wafra M 1995 Aggregation and sedimentation in colloidal suspensions *Phys. Rev. Lett.* **74** 1478–81

[5] Poon W C K, Starrs L, Meeker S P, Moussaïd A, Evans R M L, Pusey P N and Robins M M 1999 Delayed sedimentation of transient gels in colloid–polymer mixtures: dark-field observation, rheology and dynamic light scattering studies *Faraday Discuss.* **112** 143–54

[6] Verhaegh N A M, Asnaghi D and Lekkerkerker H N W 1999 Transient gels in colloid–polymer mixtures studied with fluorescence confocal scanning laser microscopy *Physica* A **264** 64–74

[7] Faers M A and Kneebone G R 1999 Application of rheological measurements for probing the sedimentation of flowables *Pesticide Sci.* **55** 312–25

[8] Stöber W, Fink A and Bohn E 1968 Controlled growth of monodisperse silica spheres in the micron size range *J. Colloid Interface Sci.* **26** 62–9

[9] Bogush G H, Tracy M A and Zukoski C F 1988 Preparation of monodisperse silica particles—control of size and mass fraction *J. Non-Cryst. Solids* **104** 95–106

[10] Edwards J, Lenon S, Toussaint A F and Vincent B 1984 Preparation and stability of polymer-grafted silica dispersions *ACS Symp. Ser.* **240** 281–96

[11] Weeks J R 2000 The steric stabilisation of colloidal particles in non-aqueous media *PhD Thesis* University of Bristol

[12] Vincent B 1993 The preparation of colloidal particles having (post-grafted) terminally-attached polymer chains *Chem. Eng. Sci.* **48** 429–36

[13] Weeks J R, van Duijneveldt J S and Vincent B 2000 Aggregation of sterically stabilised particles, unpublished

[14] Baxter R J 1968 Percus–Yevick equation for hard spheres with surface adhesion *J. Chem. Phys.* **49** 2770–4

[15] Senis D and Allain C 1997 Scaling analysis of sediment equilibrium in aggregated colloidal suspensions *Phys. Rev.* E **55** 7797–800

[16] Potanin A A and Russel W B 1996 Fractal model of consolidation of weakly aggregated colloidal dispersions *Phys. Rev.* E **53** 3702–9

[17] Starrs L 1999 Collapse of transient gels in colloid–polymer mixtures *PhD Thesis* University of Edinburgh

[18] Ruths M, Johannsmann D, Rühe J and Knoll W 2000 Repulsive forces and relaxation on compression of entangled, polydisperse polystyrene brushes *Macromolecules* **33** 3860–70

[19] Castaing J C, Allain C, Auroy P, Auvray L and Pouchelon A 1996 Nanosized hairy grains: a model system to understand the reinforcement *Europhys. Lett.* **36** 153–8

[20] van der Beek G P, Cohen Stuart M A, Fleer G J and Hofman J E 1991 Segmental adsorption energies for polymers on silica and alumina *Macromolecules* **24** 6600–11