



HAL
open science

Phase separation in mixtures of two sizes of silica particles dispersed in DMF on the addition of polystyrene

Juan Zhou, Jeroen S van Duijneveldt, Brian Vincent

► **To cite this version:**

Juan Zhou, Jeroen S van Duijneveldt, Brian Vincent. Phase separation in mixtures of two sizes of silica particles dispersed in DMF on the addition of polystyrene. *Molecular Physics*, 2011, pp.1. 10.1080/00268976.2011.554331 . hal-00686164

HAL Id: hal-00686164

<https://hal.science/hal-00686164>

Submitted on 8 Apr 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Phase separation in mixtures of two sizes of silica particles dispersed in DMF on the addition of polystyrene

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2010-0427.R1
Manuscript Type:	Special Issue paper - In honour of Bob Evans
Date Submitted by the Author:	17-Dec-2010
Complete List of Authors:	Zhou, Juan; University of Bristol van Duijneveldt, Jeroen; University of Bristol Vincent, Brian; University of Bristol
Keywords:	colloidal phase separation, depletion interaction, silica particles

SCHOLARONE™
Manuscripts

Phase separation in mixtures of two sizes of silica particles dispersed in DMF on the addition of polystyrene

Juan Zhou, Jeroen S. van Duijneveldt* and Brian Vincent.

School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK.

Abstract

Phase separation, induced by attractive depletion interactions, in mixtures of two sizes of charged silica particles (30 and 200 nm diameter), dispersed in dimethylformamide (DMF), upon the addition of a non-adsorbing, monodispersed polymer (polystyrene) has been studied, for two polymer molecular weights (number-average 115,000 and 543,000). The repulsive electrostatic interaction between the silica particles was reduced through addition of 40 mM lithium chloride. This paper is a follow-up to a recent short communication by the same authors, (*Zhou, J.; van Duijneveldt, J.; Vincent, B. Phys. Chem. Chem. Phys. 2010, 13, 110-113*), for the same silica particles, plus the lower molecular weight polymer, in DMF. In that paper we reported that, for certain concentration ranges of the ternary system, three co-existing phases are formed at equilibrium, and in others two. In this paper we show that, **despite the well-known importance of the polymer / colloid size ratio on the phase behaviour of their mixtures**, using the higher molecular weight polymer leads to broadly similar behavior, although the phase boundaries are shifted slightly. **The main new finding is that of distinct regions in the phase separation process for systems resulting in two co-existing equilibrium phases (fluid + solid). On increase of polymer concentration, initially only the large particles aggregate. At higher polymer concentration, mixed aggregates are formed consisting of both large and small particles. Whilst this finding can be rationalised in terms of relative strengths of depletion interactions, such scenarios have not been predicted theoretically to our knowledge.**

Keywords: colloidal phase separation, depletion interaction, silica particles

* corresponding author e-mail: j.s.van-duijneveldt@bris.ac.uk

1. Introduction

The addition of a non-adsorbing polymer to a colloidal suspension is known to induce depletion attraction between the constituent colloidal particles [1-4]. The first theoretical description of the depletion effect was given by Asakura and Oosawa [1, 2]. This was subsequently developed by Vrij [3]. A significant body of theoretical work is now available on depletion interactions in the so-called “colloid limit”, i.e. $q < 1$, where q is the ratio of twice the polymer radius of gyration (R_g) to the particle diameter (σ). Corresponding theoretical phase diagrams have been constructed using a variety of theoretical approaches, including perturbation theory [5], free volume theory [6], density functional theory [7], and Monte Carlo simulation [8-10]. A large body of complementary experimental work on depletion-induced aggregation and phase separation also exists. The use of hard-sphere particles has been favored in these studies as these are easiest to model. De Hek and Vrij performed experiments on model hard-sphere-like particles with added non-adsorbing polymer using the system: silica particles and polystyrene in cyclohexane [11]. The fluid-solid coexistence region of the hard-sphere system broadens on addition of polymer; whilst the fluid-fluid transition is less prominent. These observations were explained semi-quantitatively using thermodynamic perturbation theory [5]. The coexistence between two stable fluid phases, as well as fluid-solid phases, was observed for similar systems by Vincent et al. [12,13]. The polymer partitioning between the coexisting colloid-poor and colloid-rich phases was first described by the free-volume theory (FVT) of Lekkerkerker et al. [6]. These theoretical models predict a co-existence region between a colloidal crystal and a colloidal fluid for $q < 0.3$, whilst for $q > 0.3$ a fluid-fluid coexistence region also appears in the phase diagram. These theoretically predicted phase diagrams have been confirmed by simulation [8,14] and experiments [11,15-19]. The regime where the polymer coils are larger than the colloidal particles ($q > 1$) is referred to as the protein limit [20]. A major, recent paper reviewing this field and extending the FVT across a wide range of q values, as well as including the effect of solvent quality for the polymer, is that by Fleer and Tuinier [4].

For charged particles the phase behavior is modified; the additional interparticle repulsion offsets the attraction induced by added polymer. Only a few experimental results are available to date. Gögelein has presented a detailed quantitative study of cluster aggregation kinetics in charge-stabilized aqueous silica suspensions, on adding non-adsorbing polymers [21]. However, in this work van der Waals attraction also contributed significantly, and the

1
2
3 aggregation observed was essentially irreversible. In two recent papers [22,23] the present
4 authors employed silica particles, dispersed in dimethylformamide (DMF), as the model
5 dispersion. Such dispersions have been used previously as model hard spheres [24,25] and
6 there appear to have been only a limited number of other studies using this particular model
7 system [26-29]. However, silica particles dispersed in DMF are charged, just as they are in
8 water. For both of the sizes of silica particles (30 nm and 200 nm diameter) used in this work,
9 their electrophoretic mobilities in DMF, at a background concentration of LiCl of 40 mM (where
10 the Debye layer thickness (κ^{-1}) = 1 nm) were $\sim 1 \times 10^8$ V s m⁻².
11
12

13
14
15
16
17 In reference [22], the van der Waals attraction energy (V_A) between the silica particles, at a
18 separation equivalent to the diameter of two DMF molecules (DMF is known to be strongly
19 bound to silica [30]), was estimated, resulting in the following values: $V_A = 0.5$ kT for the 30 nm
20 particles and 3.5 kT for the 200 nm particles. Since the average, thermal (translational) energy
21 of the particles is ~ 1.5 kT, one may expect the smaller silica particles to be stable, even in the
22 absence of any charge repulsion. For the larger particles, however, some charge repulsion
23 would seem to be necessary in order to prevent weak aggregation of the particles due to van
24 der Waals forces, prior to the addition of any polymer.
25
26
27
28
29

30
31 In the two previous papers by us on this topic [22,23] polystyrene was employed as the added,
32 non-adsorbing polymer. DMF is a near-theta (Θ) solvent for polystyrene [22]. Various
33 parameters for the two polystyrene samples used, in DMF are listed in Table 1. The polymer
34 overlap concentration (C^*) is defined as that concentration where the polymers coils in solution
35 have a volume fraction of one, and is given by equation (1) [31],
36
37
38

$$C^* = \frac{3M_w}{4\pi R_g^3 N_A} \quad (1)$$

39
40
41 where M_w is the weight-average molar mass of the polymer, R_g is its radius of gyration in the
42 solvent concerned and N_A is the Avagadro constant.
43
44
45
46
47

48
49 As discussed earlier, an important parameter in the theory of the phase behavior of particle plus
50 polymer systems is q , where $q = 2R_g/\sigma$; σ is the diameter of the particles. q values are also
51 given in Table 1, for each polymer, with respect to the small particles (q_s) and the large particles
52 (q_l).
53
54
55
56
57
58
59
60

M_n	p	R_g / nm	$C^* / (\text{mg l}^{-1})$	q_s	q_l
115,000	1.04	9.6	54	0.64	0.10
543,000	1.09	21.3	24	1.4	0.21

Table 1. Parameters for polystyrene in DMF solutions: M_n is the number-average MW; p is the polydispersity ($p = M_w/M_n$); R_g is the radius of gyration; C^* is the critical overlap concentration; q_s and q_l are the q values with respect to the small ($\sigma = 30 \text{ nm}$) and large particles ($\sigma = 200 \text{ nm}$), respectively

In the first paper [22] in this series we reported on the phase behavior of each of the two sizes of silica particles, dispersed in DMF containing 10 or 40 mM LiCl, *separately*, on the addition of polystyrene ($M_n = 115,000$), i.e. on the *binary* systems. The larger particles ($q = 0.1$, table 1) only showed fluid-solid coexisting phases, above a certain minimum added polymer concentration, whereas the smaller particles ($q = 0.64$, table 1), with increasing polymer concentration, exhibited a fluid-fluid coexistence region, prior to the onset of the fluid-solid region. Reasonably good agreement was found between the experimental phase diagrams and the theoretical predictions of Gögelein [32].

In the second paper [23] we reported some preliminary studies on the phase behavior of the corresponding *ternary* systems, i.e. on mixtures of both sizes of silica particles, dispersed in DMF containing 40 mM LiCl, on the addition of polystyrene ($M_n = 115,000$). This was the first study of a ternary system of this type that we were aware of. In that paper we reported that, for certain concentration ranges of the ternary system, three co-existing phases are formed at equilibrium. These consisted of two fluid-like phases (the first containing mostly polymer and the second mostly small particles) and a solid-like phase (containing a mixture of small and large particles). An unexpected feature was that this phase separation occurred over two distinct time periods. In the first, relatively short period a solid-like phase containing a large fraction of both sets of silica particles separated from the polymer solution. Subsequently, over a longer period of time, the second fluid phase, containing mostly the smaller particles, separated from this solid phase.

In this paper we present a fuller study of the ternary systems. We show that using the higher molecular weight polymer (543,000) leads to broadly similar behavior as with lower molecular weight polymer (115,000) used before [22,23], although the phase boundaries are shifted slightly. More importantly, however, we have gained further insight into the compositions and

natures of the evolving phases. As far as we are aware, there is, as yet, no theoretical treatment for phase separation in ternary systems of dispersions of two different sized particles, plus non-adsorbing polymer.

2. Experimental

2.1 Materials

The solvent used in all experiments was dimethylformamide (DMF), supplied in “dry” form by Aldrich (Anhydrous, 99.8%). Two sizes of silica particles were used. The first sample (diameter from dynamic light scattering [22] 30 nm) was supplied as an aqueous dispersion by AZ Electronics (Klebosol 30R25). The second sample (diameter from dynamic light scattering [22] 200 nm) was obtained in powder form from Blue Helix Ltd. (Fibre Optic Centre Inc.). One polystyrene (PS) sample, $M_n = 115,000$, was obtained from Polymer Source (Sample no. P5015-S). The second polystyrene sample, $M_n = 543,000$, was also obtained from Polymer Source (Sample no. P2577-St). The polydispersity factors are given in Table 1. Lithium chloride (LiCl) from Fisher Scientific was used as supplied.

2.2 Silica dispersions and polymer solutions in DMF

Dispersions of the 200 nm particles in DMF were prepared by adding the silica powder to the solvent in the required amounts, followed by application of ultrasound (Ultrawave Ltd. Cardiff), for 6 h, to break up any aggregates. For the 30 nm particles transfer from water to DMF was achieved using a dialysis technique, as described in reference [22].

The transmission electron microscope diameters, the mean hydrodynamic diameters and the mean electrophoretic mobilities of the two grades of silica particles in DMF have all been presented in reference [22]. Dynamic light scattering studies led to values of 30 nm and 200 nm for the hydrodynamic diameters for the two grades of silica particles in DMF.

Since DMF is known to be a hygroscopic solvent, it was important to estimate how much water might be present in samples prepared for the phase behavior studies, prior to sealing the sample tube. It was reported in reference [22] that the maximum amount of water in the DMF solutions was never greater than 1% (by wt), and that at 1 % water in DMF the hydrodynamic diameter of the PS molecules was found to be unchanged compared to PS solutions in DMF which had been vigorously dried. So it seemed reasonable to assume that, at these low levels

1
2
3 of water present in the DMF, there was also no effect on the thermodynamic properties of the
4 polymer solutions.
5
6
7

8 9 **2.3 Visual Observation of Phase Behavior**

10
11 Samples were prepared by addition of polystyrene and LiCl to mixtures of the silica dispersions,
12 in the required amounts. The sample cells were then sealed with Teflon stoppers and PTFE
13 tape. The cells were very slowly tumbled, around their long axis, overnight and then left to
14 stand. Any phase separation usually started quickly and was complete within a few hours.
15
16
17

18 19 **2.4 Differential Interference Contrast Microscopy**

20
21 Differential interference contrast (DIC) microscopy was performed on several of the samples
22 that had reached phase equilibrium. This technique is highly sensitive to refractive index
23 differences across a sample in the focal plane of the microscope. An Olympus BX51
24 microscope was used with a Pixelink 5MP colour CCD camera PL-B625CU. To this end, after
25 vigorously shaking (by hand) a particular sample in its cell, a small drop was placed between
26 two cover slips and mounted in the microscope. The shaking procedure was carried out to re-
27 homogenize the sample, as effectively as possible. The phase separation could then be
28 followed in time, and pictures taken at set time intervals.
29
30
31
32
33

34 35 **2.5 Analysis of Phase Compositions**

36
37 For the samples where phase separation had occurred, each phase was analyzed to determine
38 its equilibrium large and small silica particle and polystyrene concentrations after 24 h. This was
39 achieved as follows. Firstly a photograph was taken of the (flat) cell to determine the volume of
40 each phase. For those systems which had separated into three phases the following procedure
41 was used. A sample of the top phase was removed and analyzed for its polystyrene
42 concentration using UV-visible spectroscopy. A peak in the spectrum was chosen where only
43 polystyrene absorbed and silica did not. A calibration graph was established at this wavelength
44 (274 nm). A sample of the middle phase was also removed and analyzed for its polystyrene
45 concentration. The concentration of polystyrene in the bottom phase could then be calculated by
46 difference, knowing the total initial amount added. The concentration of the larger (200 nm)
47 silica particles in each of the top two phases could also similarly be determined using UV-visible
48 spectroscopy, but now at a wavelength where polystyrene did not adsorb (500 nm). This could
49 be achieved because it had been shown that the contribution from smaller (30 nm) silica
50
51
52
53
54
55
56
57
58
59
60

particles was negligible by comparison. The concentration of larger particles in the bottom phase could also be calculated by difference. Known volumes of all three phases were then removed, the DMF evaporated, and the mass of solid remaining was determined in each case. The total concentration of silica in each of the three phases could then be calculated by subtracting the calculated contribution from polystyrene present in each case. Similarly, since the concentration of large particles in each of the three phases was also known from the UV-visible spectroscopy experiments, it was possible to calculate, by difference, the concentration of small silica particles in each of the three phases.

2.6 Transmission Electron Microscopy (TEM)

In order to obtain semi-quantitative information regarding the relative concentrations of the two sizes of silica particles in each phase at equilibrium, transmission electron micrographs were obtained of those phases containing significant concentrations of silica particles (i.e. the lower phase in a two-phase system or the two lowest phases in a three-phase system). This was achieved by spotting samples of each phase concerned on a TEM grid, allowing the DMF to evaporate, and using a JEOL TEM 1200EX instrument to take the micrographs.

3 Results and Discussion

3.1 Phase Diagrams

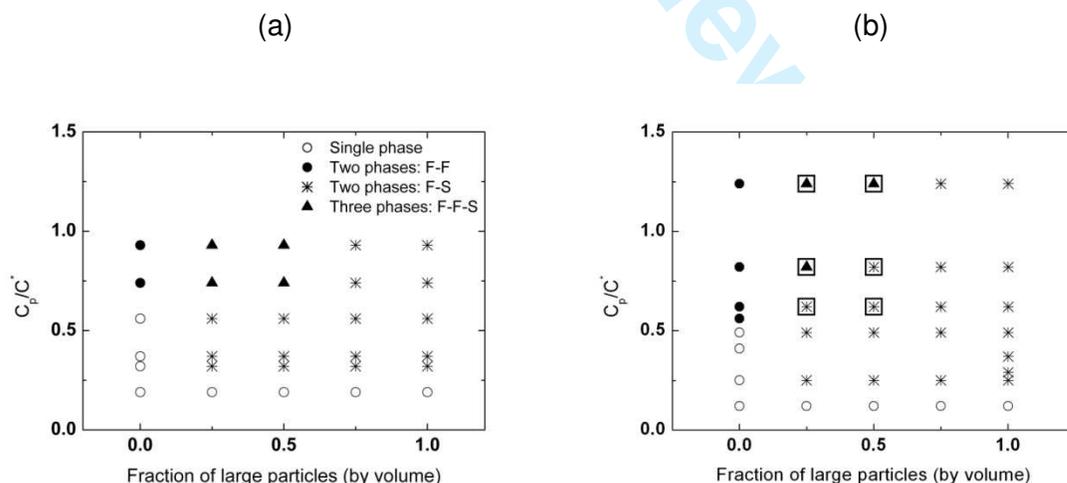


Figure 1. Phase diagrams for dispersions of mixtures of 30 nm and 200 nm silica particles, dispersed in DMF plus 40 M LiCl, at an overall particle volume fraction of 0.12, plus added polystyrene: (a) $M_n = 115,000$; (b) $M_n = 543,000$ (see Table 1). (The symbols with boxes are explained later in the text, §3.2 and Figure 3).

1
2
3 As may be seen from Figure 1, the 200 nm particles, on their own, only show a fluid-solid
4 coexistence region above a certain C_p/C^* value, whereas for the 30 nm particles on their own a
5 fluid-fluid coexistence region is formed. We showed in Ref. [22] that at higher C_p/C^* values a
6 solid-fluid region also exists for the 30 nm particles. For the 30 nm particles alone, the onset of
7 the fluid-fluid region seems to occur at a slightly lower value of C_p/C^* for the higher molecular
8 weight polymer. It is difficult to say whether this is to be expected on theoretical grounds, as the
9 presence of the interparticle electrostatic forces (even in the presence of 40 mM LiCl, where κ^{-1}
10 = 1 nm) complicates the theoretical treatment. The theoretical work by Gögelein and Tuinier [32]
11 suggests that, if anything, a slightly higher polymer concentration would be required for the
12 larger polymer. Note however that this comparison requires knowledge of C^* , which is difficult to
13 estimate accurately (it depends on R_g^3 , for example - equation [1]). It is also not possible to say,
14 from the results shown in Figure 1, whether there is any real effect of polymer molecular weight
15 on the value of C_p/C^* where phase separation starts for the 200 nm particles, or indeed for any
16 of the particle mixtures studied.
17
18
19
20
21
22
23
24
25
26

27 Also from Figure 1, it may be seen that, for the mixed particle systems, when the fraction of the
28 large particles is 0.25 or 0.5, then with increasing C_p/C^* values, firstly a region of two-phase
29 (fluid-solid) coexistence is observed, followed by a region of *three-phase* coexistence, at
30 equilibrium, for both polymer molecular weights. We reported in Ref. [23] the unexpected way in
31 which the three-phase region evolves with time. Firstly, over a period of minutes, a two-phase
32 (fluid-solid) system forms, with virtually all the polymer in the upper fluid phase and all the
33 particles (large and small) in the lower solid phase. Then over a period of hours, a second fluid
34 phase, containing a proportion of the small particles, separates from the lower solid phase,
35 where the remainder of the small particles and virtually all of the large particles remain. **In
36 summary, despite the well-known importance of the polymer / colloid size ratio on the phase
37 behaviour of their mixtures, using the higher molecular weight polymer leads to broadly similar
38 behavior, although the phase boundaries are shifted slightly.**
39
40
41
42
43
44
45
46

47 It is known [33] that, for a given C_p value, for two sizes of particles, the depletion interaction
48 decreases in the order: large-large > large-small > small-small. On this basis we would
49 postulate that with increasing C_p/C^* value, we should see the order of phase separation of the
50 particles depicted schematically in Figure 2.
51
52
53
54
55
56
57
58
59
60

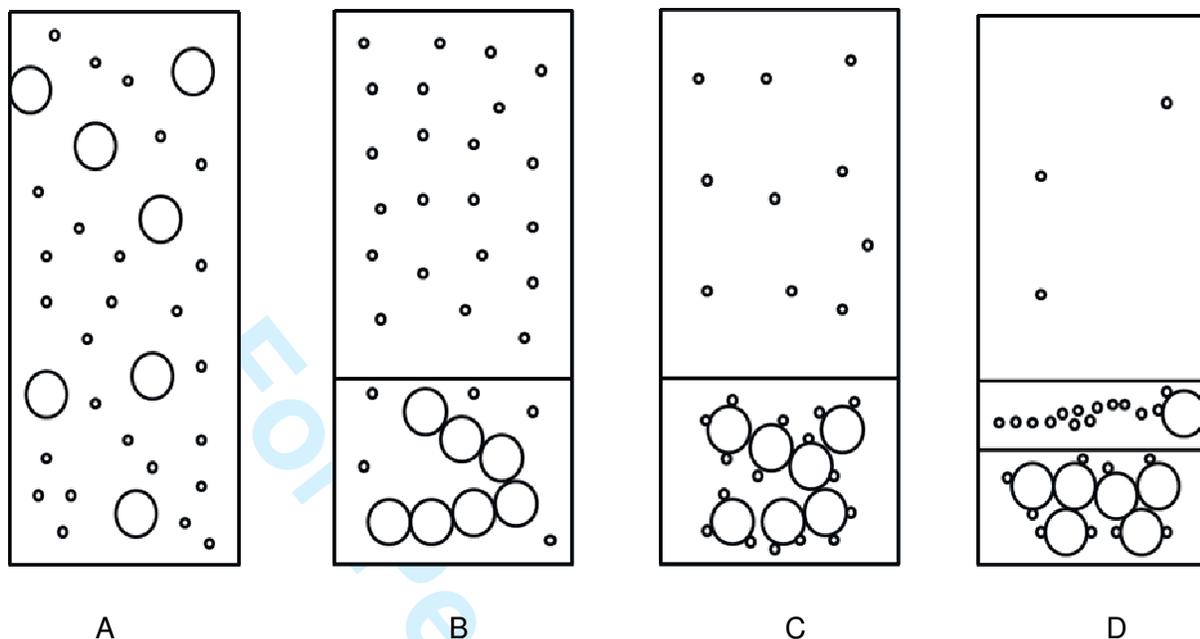


Figure 2. Schematic representation of the evolution of phase separation of the large and small particles, with increasing added polymer concentration (from left to right).

Some of these schematic phase-separated systems are to be found in Figure 1 for the mixed particle dispersions. State A (stable one-phase system) is represented by the open circles in Figure 1, and state D (two aggregated phases: one a solid phase containing large-large and large-small aggregates, and the second a liquid phase containing weakly aggregated small particles) by the filled triangles. The two-phase (solid-fluid) systems represented by the crosses in Figure 1 could correspond to state B or C in Figure 2. It is difficult to distinguish these two states from simple observations of the phase behavior. Later in this paper we will present other evidence, i.e. analysis of the phase compositions and TEM studies, from which we can distinguish these two states.

3.2 Differential Interference Contrast Microscopy Experiment

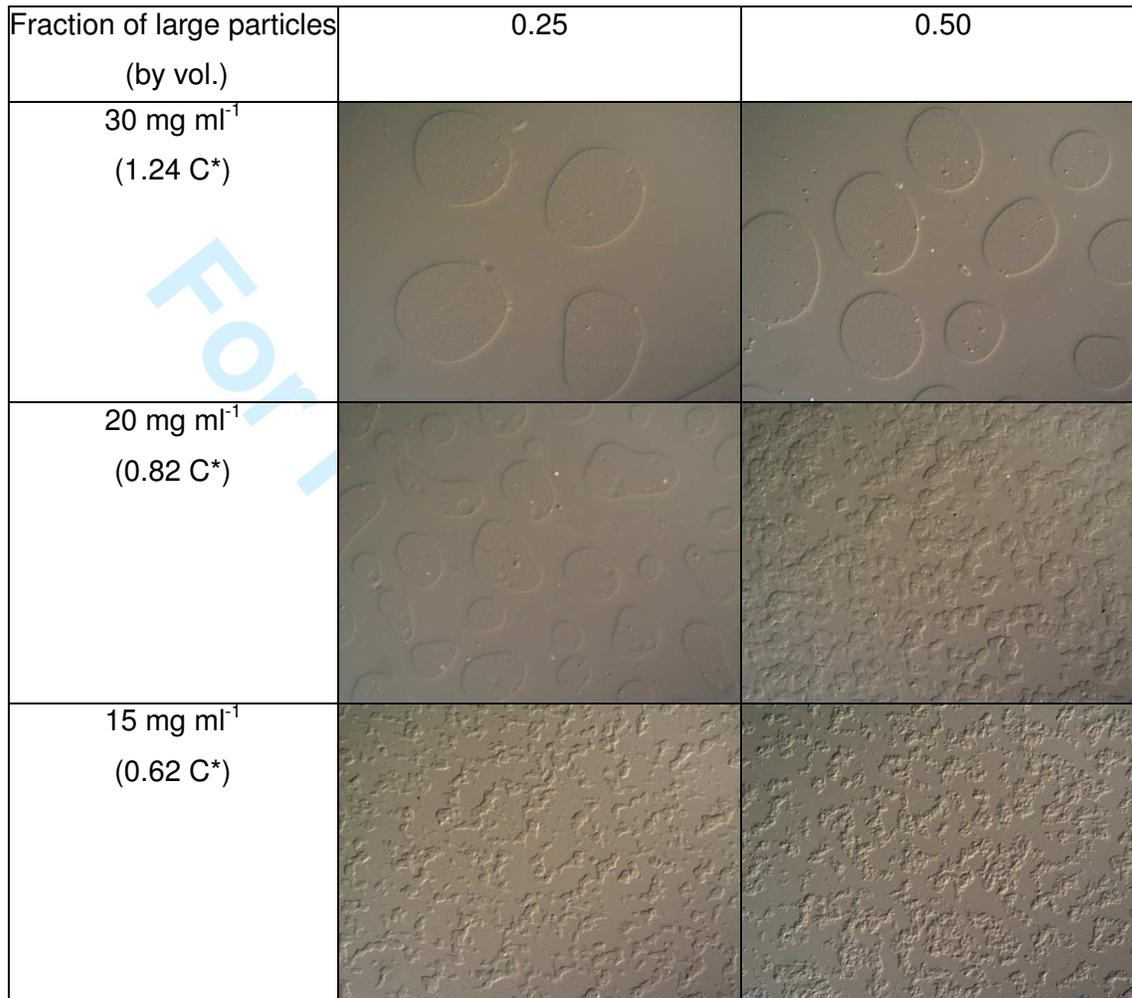


Figure 3. DIC microscopy images of the systems indicated by the boxed symbols in Figure 1. Images are taken 2 min after mixing. The width of each image is 475 μm .

Figure 3 shows typical DIC images of some of the systems taken 2 min after mixing the dispersions with the higher molecular weight polymer. These are broadly similar to the images we reported in Ref. [23] for the lower molecular weight polymer, but these new DIC images are included here to back-up the comments made in the previous section, regarding the nature of the observed phases and how they form. For the three systems which form three-phases at equilibrium (indicated by the boxed, filled triangles in Figure 1 and state D in Figure 2), after two minutes we see fluid droplets of the (eventual) middle phase, i.e. consisting of the small-small weak aggregates (not actually visible at this magnification). However, these droplets also initially contain the (visible) aggregates made of large-large and large-small contacts. It seems that

initially all the particles that are going to aggregate first separate from the polymer solution, which forms the continuous phase (and presumably also contains a small percentage of non-aggregated particles). Slowly, with time, the aggregates of large-large and large-small contacts separate from the small-small contacts, and settle to form a consolidated solid phase at the bottom of the vessel, to leave the middle liquid phase containing weak aggregates comprising small-small contacts.

The three other DIC images shown in Figure 3, show no droplets, only aggregates, and correspond to the two-phase equilibrium systems (boxed crosses) shown in Figure 1. We are not able at this point to distinguish whether these correspond to state B or C in Figure 2. We need additional evidence to make this distinction; this is discussed in the next section.

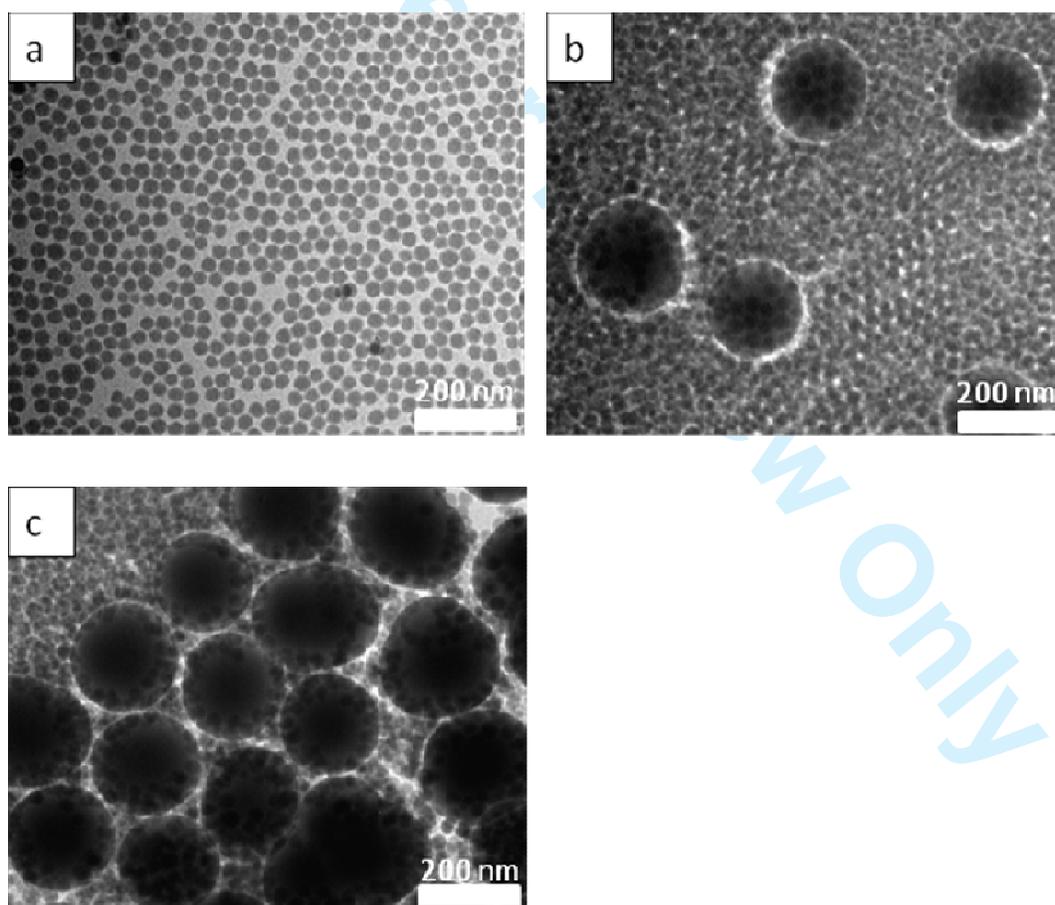
3.3 Analysis of Phase Compositions and Transmission Electron Microscopy

In Table 2 below we present some data obtained by analyzing the composition of each of the coexisting phases for some of the mixtures studied. These values are only an approximate guide, as their accuracy is limited, both by the sensitivity of the techniques used, and the fact that some of the particles were found to adhere to the walls of the tubes.

fraction of large particles:		0.25			0.75		
C_p/C^*	phase	C_p /(mg l ⁻¹)	C_{small} /(mg l ⁻¹)	C_{large} /(mg l ⁻¹)	C_p /(mg l ⁻¹)	C_{small} /(mg l ⁻¹)	C_{large} /(mg l ⁻¹)
0.74	top	55	19	0	-		
	middle	23	510	38			
	bottom	3	700	380			
0.56	upper	28	200	0	-		
	lower	*	440	370			
0.37	upper	16	210	0	-		
	lower	*	420	530			
0.28	upper	19	210	0	20	80	0
	lower	0	440	530	0	26	980

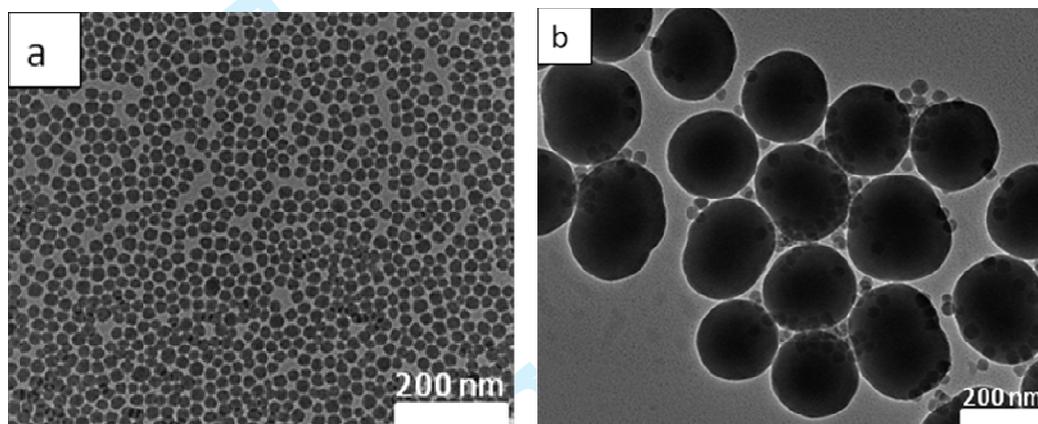
1
2
3 Table 2. Analysis of phase compositions for two fractions of large particles in mixtures of large
4 and small particles, plus the lower molecular weight polystyrene (115,000). (* too inaccurate to
5 quote).
6
7

8
9 Nevertheless, some insight may be gained from comparing the values in this table. Firstly, in the
10 three-phase coexistence system at 0.25 fraction of large particles, and C_p/C^* 0.74, a large
11 concentration of the small particles is to be found, not only in the middle (fluid) phase, but also
12 in the bottom (solid) phase. There is also a small concentration of (stable) small silica particles
13 in the top phase. This is consistent with the schematic sketch D in Figure 2 and also with TEM
14 pictures shown in Figure 4. Please note that the absolute concentrations of large and small
15 particles shown is not reliable, because of drying artifacts, but the relative concentrations of
16 small and large particles are significant.
17
18
19
20
21
22



53
54 Figure 4. TEM pictures of the three coexisting phases for the 0.25 fraction of large particles and
55 C_p/C^* 0.74 system ($M_n = 115,000$): (a) is the top (stable, fluid) phase, (b) is the middle (fluid)
56 phase, and (c) is the bottom (solid) phase.
57
58
59
60

1
2
3 At lower C_p/C^* values for the 0.25 fraction of large particles systems, there is a larger
4 concentration of small particles in the lower phase than in the upper phase; this is consistent
5 with sketch C in Figure 2. However, for the 0.75 fraction of larger particles system, at C_p/C^* of
6 0.28, there is a larger concentration of small particles in the upper (stable fluid) phase. This is
7 more consistent with Sketch B in Figure 2. A TEM picture of the 0.75 fraction of larger particles
8 system, at C_p/C^* of 0.28, is shown in Figure 5. This is also consistent with sketch B in Figure 2.
9
10
11
12
13



29 Figure 5. TEM pictures of the 0.75 fraction of larger particles system, at C_p/C^* of 0.28 ($M_n =$
30 115,000): (a) is the upper phase; (b) is the lower phase.
31
32

33 4 Conclusions

34
35 Our observations provide evidence for the existence of each of the four systems (A-D) sketched
36 in Figure 2. In particular, in this paper we have been able to distinguish the separate existence
37 of states B and C. Although we suspect that there will be a sharp transition between these two
38 states, as the polymer concentration is increased, at certain particle size and concentration
39 ratios, it would be good to investigate whether this claim can be justified on theoretical grounds.
40
41
42
43

44 5 Acknowledgments

45
46 We should like to thank AkzoNobel and EPSRC for the provision of a Dorothy Hodgkin research
47 studentship for JZ, and Simon Davies and Simon Emmett of AkzoNobel for helpful discussions.
48
49
50
51
52
53
54
55

56 References

57
58
59
60

- 1
2
3 [1] S. Asakura and F. Oosawa, *J. Chem. Phys.* **22**, 1255 (1954).
4
5 [2] S. Asakura and F. Oosawa, *J. Polym. Sci.* **33**, 183 (1958).
6
7 [3] A. Vrij, *Pure Appl. Chem.* **48**, 471 (1976).
8
9 [4] G. J. Fleer and R. Tuinier, *Adv. Colloid Interface Sci.* **143**, 1 (2008).
10
11 [5] A. P. Gast, C. K. Hall and W. B. Russel, *J. Colloid Interface Sci.* **96**, 251 (1983).
12
13 [6] H. N. W. Lekkerkerker, W. C. K. Poon, P. N. Pusey, A. Stroobants and P. B. Warren,
14 *Europhys. Lett.* **20**, 559 (1992).
15
16 [7] M. Schmidt, H. Lowen, J. M. Brader and R. Evans, *Phys. Rev. Lett.* **85**, 1934 (2000).
17
18 [8] M. Dijkstra, J. M. Brader and R. Evans, *J. Phys. : Condens. Matter* **11**, 10079 (1999).
19
20 [9] P. G. Bolhuis, A. A. Louis and J. P. Hansen, *Phys. Rev. Lett.* **89**, 128302 (2002).
21
22 [10] R. L. C. Vink, J. Horbach and K. Binder, *Phys. Rev. E* **71**, 051406 (2005).
23
24 [11] H. De Hek and A. Vrij, *J. Colloid Interface Sci.* **84**, 409 (1981).
25
26 [12] B. Vincent, *Colloids Surf.* **24**, 269 (1987).
27
28 [13] B. Vincent, J. Edwards, S. Emmett and R. Croot, *Colloids Surf.* **31**, 267 (1988).
29
30 [14] E. J. Meijer and D. Frenkel, *J. Chem. Phys.* **100**, 6873 (1994).
31
32 [15] C. Cowell, R. Li-In-On and B. Vincent, *J. Chem. Soc., Faraday Trans. 1* **74**, 337 (1978).
33
34 [16] F. L. Calderon, J. Bibette and J. Biais, *Europhys. Lett.* **23**, 653 (1993).
35
36 [17] W. C. K. Poon *et al.*, *J. Phys. II* **3**, 1075 (1993).
37
38 [18] S. M. Ilett, A. Orrock, W. C. K. Poon and P. N. Pusey, *Phys. Rev. E* **51**, 1344 (1995).
39
40 [19] W. C. K. Poon, *J. Phys. : Condens. Matter* **14**, R859 (2002).
41
42 [20] K. J. Mutch, J. S. van Duijneveldt and J. Eastoe, *Soft Matter* **3**, 155 (2007).
43
44 [21] C. Gögelein, G. Nagele, J. Buitenhuis, R. Tuinier and J. K. G. Dhont, *J. Chem. Phys.* **130**,
45 204905 (2009).
46
47 [22] J. Zhou, J. S. van Duijneveldt and B. Vincent, *Langmuir* **26**, 9397 (2010).
48
49 [23] J. Zhou, J. S. van Duijneveldt and B. Vincent, *Phys. Chem. Chem. Phys.* **13**, 110 (2011).
50
51 [24] A. Imhof and J. K. G. Dhont, *Phys. Rev. Lett.* **75**, 1662 (1995).
52
53 [25] A. Imhof and J. K. G. Dhont, *Colloids Surf., A* **122**, 53 (1997).
54
55 [26] C. Vonk, S. M. Oversteegen and J. Wijnhoven, *J. Colloid Interface Sci.* **287**, 521 (2005).
56
57 [27] G. A. Vliegenthart, A. van Blaaderen and H. N. W. Lekkerkerker, *Faraday Discuss.* **112**,
58 173 (1999).
59
60 [28] G. A. Vliegenthart, and H. N. W. Lekkerkerker, *J. Chem. Phys.* **111**, 4153 (1999).
[29] G. H. Koenderink, G. A. Vliegenthart, S. Kluijtmans, A. van Blaaderen, A. P. Philipse and H.
N. W. Lekkerkerker, *Langmuir* **15**, 4693 (1999).
[30] G. P. van der Beer, M. A. Cohen Stuart and T. Cosgrove, *Langmuir* **7**, 327 (1991).

1
2
3 [31] P. G. de Gennes, *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca,
4 NY, 1979.

5
6 [32] C. Gögelein and R. Tuinier, *Eur. Phys. J. E.* **27**, 171 (2008).

7
8 [33] S. Rawson, K. Ryan and B. Vincent, *Colloids Surf.* **34**, 89 (1988).
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Peer Review Only