

SUPPLEMENTARY INFORMATION

(1) Video Showing the time evolution of the three samples presented in Figure 2.

(2) Experimental Details

(3) TEM Images

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 (diameter ~30 nm) was supplied as an aqueous dispersion by AZ Electronics (Klebosol 30R25). The second (diameter ~200 nm) was obtained in powder form from Blue Helix Ltd. (Fibre Optic Centre Inc.). Transmission electron microscope (JEOL TEM 1200EX) images have been shown in a previous paper by us.¹ Polystyrene was obtained from Polymer Source (Sample#P5015-S); its number average molecular weight (M_n) and weight molecular weight (M_w) were $115,000 \text{ g mol}^{-1}$ and $119,600 \text{ g mol}^{-1}$, respectively; hence $M_w/M_n = 1.04$. Lithium chloride (LiCl) from Fisher Scientific was used as supplied.

Silica Dispersion Preparation and Characterisation

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, 6 hours) to break up any aggregates. For the 30 nm particles, transfer from water to DMF, as the dispersion medium, was required. This was achieved using a dialysis technique. The dialysis tubing used (with a molecular weight “cut-off” of 12–14,000 Da) was supplied by Medicell International Ltd; it was boiled in water several times before use. The aqueous silica dispersion was then placed inside the tube, which was then in turn placed in DMF, such that the relative volumes of DMF to water were 50 ml aqueous silica sol inside the tube

against 500 ml DMF externally. The DMF solvent was changed every day until the refractive index of the final DMF external phase acquired the same value as that for pure DMF, as determined using an Abbe refractometer.

The mean hydrodynamic diameters of the two grades of silica particles in DMF were obtained using dynamic light scattering (Malvern Autosizer 4800), giving mean values of 30 nm and 200 nm, respectively. The electrophoretic mobilities of the silica particles were determined with a Zeta Plus (Zeta potential Analyzer, Brookhaven instruments corporation) instrument, using its phase analysis fitting program. Mean values of -1.66 and -2.0×10^8 V s m^{-2} were obtained for the 30 and 200 nm particles, respectively, in pure DMF.⁴ In solutions of 40 mM LiCl in DMF, the corresponding mean values were -1.08 and -1.30×10^8 V s m^{-2} , respectively. Dispersions of both sets of silica particles were observed to be stable in 40 mM LiCl in DMF solutions.¹ This is to be expected given the magnitude of the electrophoretic mobility values obtained.

Since DMF is known to be a hygroscopic solvent, it was important to know how much water might be present in a typical sample prepared for the phase behaviour studies, prior to sealing the sample tube. In a previous study with these same systems we had investigated this point.¹ The amount of water found to be present was never greater than 1% (by wt). We also studied previously⁴ the effect of added water on the solubility of polystyrene in DMF. It was found that polystyrene began to precipitate from solution at approximate 3% (by wt) water content.

Visual Observation of Phase Behaviour

Samples were prepared, in flat optical cells, by firstly adding polystyrene powder, then DMF, then the stock silica dispersions in DMF, and finally LiCl solution in DMF, in such amounts that the total concentration of silica particles was always 12% by volume, the LiCl concentration was always 40 mM, and the polymer concentration varied up to 50 mg ml⁻¹.

The following ratios (by volume) of small particles to large particles were used: 3 to 1, 1 to 1 and 1 to 3. The sample cells were then sealed with Teflon stoppers and PTFE tape. The cells were very slowly tumbled, around their long axis, overnight and then left to stand. Any phase separation usually started quickly and was complete within 24 h.

Differential Interference Contrast Microscopy

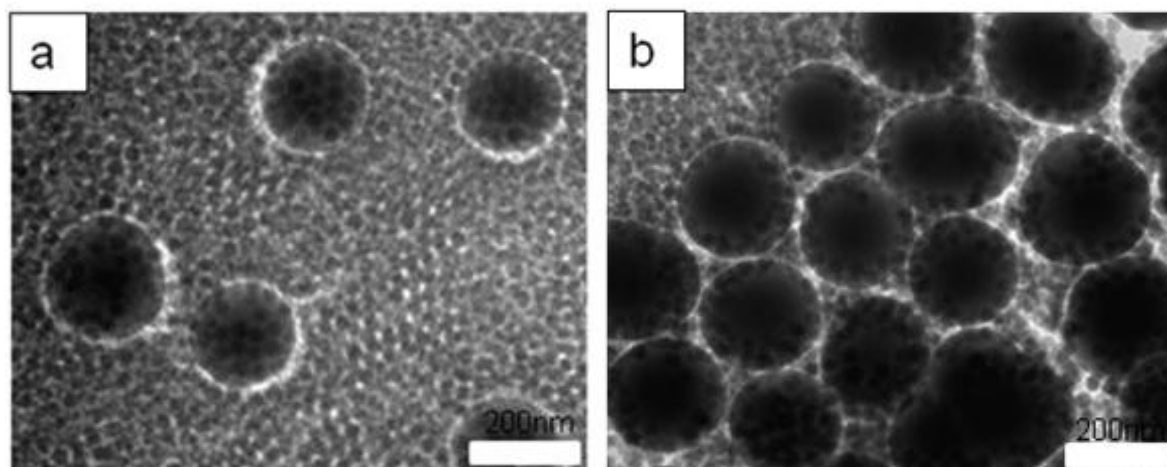
Differential interference contrast (DIC) microscopy was performed on several of the samples that had reached phase equilibrium. This technique is highly sensitive to refractive index differences across a sample in the focal plane of the microscope. An Olympus BX51 optical microscope, with Pixelink PL-B625CU 2592 x 1944 pixels, CMOS colour camera attachment, was used. To this end, after vigorously shaking (by hand) a particular sample in its cell, a small drop was placed between two cover slips and mounted in the microscope. The shaking procedure was carried out to re-homogenise the sample, as effectively as possible. The phase separation could then be followed in time, and images taken at set time intervals.

Analysis of Phase Compositions

For the samples where phase separation had occurred, each phase was analysed to determine its equilibrium large and small silica particle and polystyrene concentrations, i.e. after 24 h. This was achieved as follows. Firstly a photograph was taken of the (flat) cell to determine the volume of each phase. For those systems which had separated into three phases the following procedure was used. A sample of the top phase was removed after 24 h and analysed for its polystyrene concentration using UV-visible spectroscopy. A peak in the spectrum was chosen where only polystyrene absorbed and silica did not. A calibration graph was established at this wavelength (274 nm). A sample of the middle phase was also removed and analysed for its polystyrene concentration. The concentration of polystyrene in the bottom phase could then be calculated by difference, knowing the total initial amount added.

The concentration of the larger (200 nm) silica particles in each of the top two phases could also similarly be determined using UV-visible spectroscopy, but now at a wavelength where polystyrene did not adsorb (500 nm). This could be achieved because it had been shown that the contribution from smaller (30 nm) silica 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.

Similar experiments were carried out on some of the same systems which had formed three phases at equilibrium, but now after only 10 min had evolved. At this point, only two phases had appeared.



TEM images for the phase-separated sample after 24 h ($C_p/C^* = 0.74$ and 1: 3 large : small particles (by vol)): (a) the middle phase; (b) the bottom phase.

References

1. J. Zhou, J. S. van Duijneveldt and B. Vincent, *Langmuir* 2010, **26**, 9397-9402.