

## Supporting Material 1

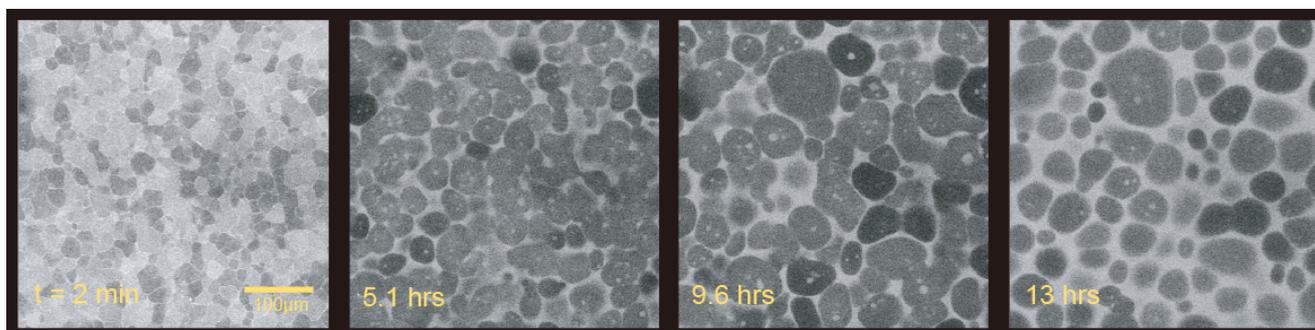
### Determination of the lateral concentration profiles of the silica (L) and PS (H) particles

Silica particles: We determined the concentration profiles of the silica particles in the binary and silica one-component systems as follows. Firstly, aqueous solutions of sodium hydroxide NaOH were added to each fractions of the samples so as to  $[\text{NaOH}] = 0.1 \text{ M moles/L}$ , and heated at  $100^\circ\text{C}$ . After 30 min, the silica particles were hydrolyzed to silica monomers (*i.e.*, silicic acid molecules  $\text{Si}(\text{OH})_4$ ). Concentrations of the resulting silicic acid,  $c$ , in each fractions were determined by a molybdenum blue method (R.J. Volk and R.L.Weintraub, *Anal.Chem.*, **1958**, *30*, 1011); aqueous solutions of molybdenum ammonium were added to the hydrolyzed samples to form yellowish molybdenum silicates complexes. Then reduction solutions composed of sodium sulfite, oxalic acid, *p*-methylphenol sulfate, sulfuric acid, and hydrochloric acid were added to the samples, whereby bluish molybdenum silicates were produced. Adsorptions of the sample solutions at wavelength = 810 nm were measured to determined the concentration of the molybdenum silicates. The particle volume fraction  $\phi$  was then determined based on a relationship  $c \text{ (ppm)} = 1.25 \times 10^3 \phi$  which was separately determined for standard samples.

PS particles: Concentrations of PS particles in the binary colloids were determined by performing turbidity measurements in 90% ethylene glycol (EG)/ water mixtures. Refractive index ( $n_r$ ) measurements of colloidal silica ( $n_r =$  approximately 1.45) in EG/water mixtures showed that the refractive index of silica was matched when EG concentration was 90%. Therefore, the turbidity of the PS + silica binary colloids in 90% EG is resulted from PS particles. 0.3 mLs of each fraction of the samples were mixed with 2.7 mL pure EG to obtain the 90% EG dispersions. The turbidity in visible wavelength regime was determined by spectrophotometer. The concentration of PS particles was determined on the bases of calibration curve separately determined for PS dispersion in 90% EG.

## Supporting Material 2

### LSM images of the phase separated structure



*Supplementary Fig. 1. Confocal laser scanning micrographs showing time evolution of the phase separation structure (taken from the bottom of the sample cell). Sample: H2 + L,  $X = 0.70$ . Here no gelation was carried out.*