Supporting Information

Solvent Structure Controlled SeedGel Formation Investigated using Miscible Binary Solvent

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Miscible binary solvent verification (h-3MP/H_2O)

Large droplets formed during the phase separation of binary solvent could scatter light strongly. A reduction of optical transmittance is usually used to characterize the phase separation temperature of a binary solvent experimentally. [1,2] Consistent with what is reported in the literature, the transmittance measurements on h-3MP/H_2O do not show a drop in transmittance (Figure S1).[1] In fact, the transmittance of light between 350 nm and 1100 nm does not show a noticeable change in the temperature range between 22 °C and 90 °C. This indicates that the solvent pair does not phase separate macroscopically.

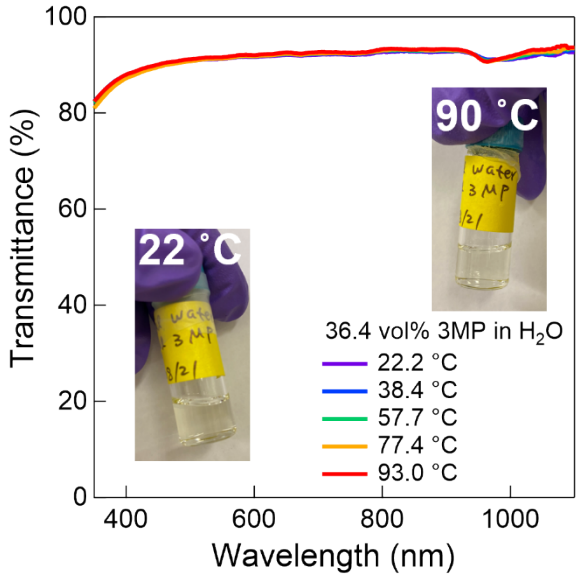

Figure S1. Transmittance measurements of hydrogenated 3-methylpyridine/H_2O mixture do not show macroscopic phase separation between 20 ˚C and 90 ˚C.

Description of the Teubner-Strey model

In the literature, the Teubner-Strey model has been implemented by researchers to fit the scattering results of bicontinuous structures. [3–5] The micro-meter domains in SeedGel can be successfully described by the Teubner-Strey model in a partially miscible binary solvent system (2,6-lutidine/ H_2O). [6,7] In this work, similar scattering features are observed in the USANS data for the miscible binary solvent system (3-methylpyridine/ H_2O), and the same model fitted the scattering results well. The scattering intensity can be mathematically written as a function of the domain volume fraction (φ_a), the contrast ($\Delta\rho$), correlation length (ξ), and the magnitude of wavevector (q) in Eq-1. The term *bkg* is the background of the scattering. The contrast is defined as the difference in scattering length density (SLD) between the two domains. Here, the variables c_1, c_2, and a_2 are expressed with the periodicity (d) and correlation length (ξ), shown from Eq-2 to Eq-4. [3–5] The

periodicity (d), correlation length (ξ), and scale are left as variables. And the rest of the parameters are fixed as constants during the model fitting. The modeled scattering curves are plotted together with the experimental results in Figure 2 in the Main text. The obtained periodicities and the correlation lengths are listed in Table 1 in the main text.

$$I(q) = \frac{8\pi\varphi_a(1-\varphi_a)(\Delta\rho)^2 c_2/\xi}{a_2 + c_1 q^2 + c_2 q^4} + bkg \quad \text{Eq-1}$$

$$c_1 = -2\xi^2\left(\frac{2\pi\xi}{d}\right)^2 + 2\xi^2 \quad \text{Eq-2}$$

$$c_2 = \xi^4 \quad \text{Eq-3}$$

$$a_2 = \left[1 + \left(\frac{2\pi\xi}{d}\right)^2\right]^2 \quad \text{Eq-4}$$

Miscible binary solvent verification (d-3MP/H_2O)

Similar to what is observed in the solvent pair h-3MP/H_2O, the transmittance measurement in 3-3MP/H_2O does not change up to about 75 °C (Figure S2). It indicates that the binary solvent of h-3MP/H_2O does not phase separate within the temperature range of interest.

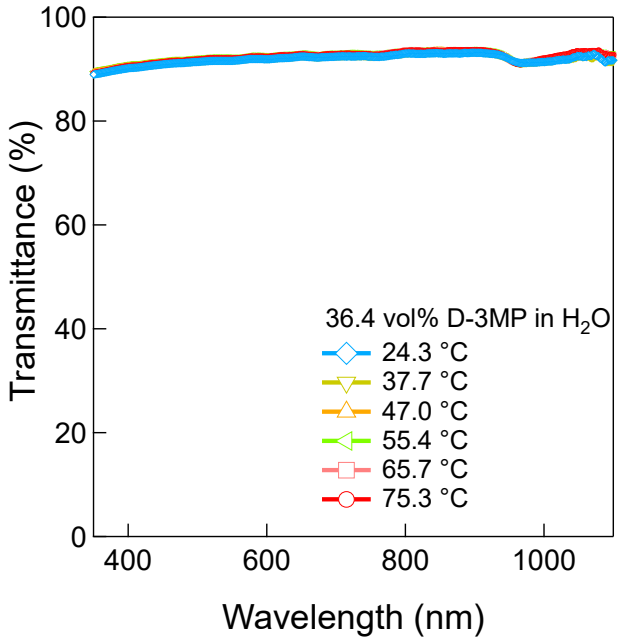

Figure S2. UV-vis measurements of deuterated 3-methylpyridine/H_2O mixture that do not show macroscopic phase separation between 20 ˚C and 80 ˚C.

Estimation of particle volume fraction in the particle domain

The Hayter-Penfold method was used to estimate the volume fraction of particles in the particle domain, as a strong charge repulsion exists between the nanoparticles. [8,9] The SAXS data at the high-q region was fitted for SeedGel prepared in h-3MP/H_2O. The form factor of the particles has been measured in the dilute solutions (0.5% in volume) in our previous work, and the nanoparticle's diameter is about 27 nm.[6] In the model, the volume fraction of the particles and the scale factor were left as variables. The rest of the parameters were kept as fixed values. [10] Figure S3(a) shows the fitting results of the SAXS data, and the extracted structure factor is plotted in Figure S3(b). The model describes the SAXS data well. The particle volume fraction in the particle domain is about 41 %, similar to the local particle concentration obtained in the particle domain of SeedGel in the 2,6-lutidine/H_2O system. [6]

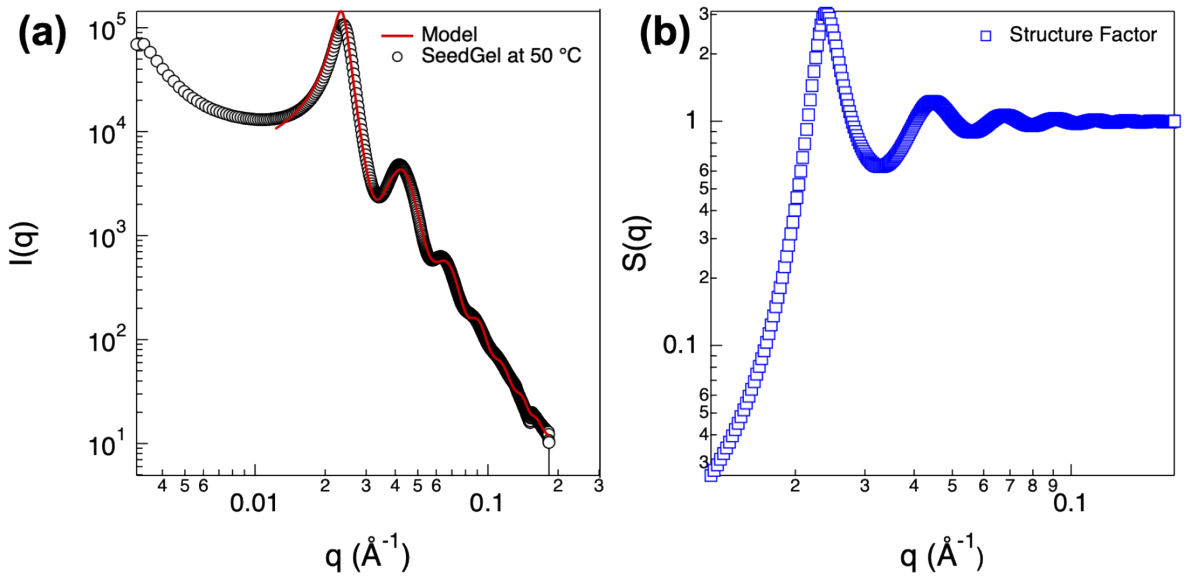

Figure S3 (a) The SAXS data of SeedGel prepared in h-3MP/H_2O system at 50 ˚C fit with Hayter-Penfold method and (b) the corresponding structure factor.

Description of the Lorentz model

The Lorentz model (Ornstein-Zernicke model) is used to obtain the correlation length in a binary solvent.[11–13] The scattering intensity can be modeled using Eq-5 below. Here, q is the magnitude of the wavevector, and L is the correlation length.

$$I(q) = \frac{scale}{1 + (qL)^2} + background \qquad \text{Eq-5}$$

SANS results of the partially miscible solvent 2,6-lutidine/D_2O

The scattering results of 2,6-lutidine/D_2O are shown in Figure S4. Starting from room temperature, the scattering intensity increases, and the hump shifts to a lower-q value when the sample is heated up. It suggests that the correlation length of the phase-separated binary solvent becomes larger and larger. When the temperature reaches 30 °C, a sudden drop in the scattering intensity is observed, which suggests a macroscopic phase separation of the binary solvent. In the

partially miscible binary solvent, SeedGel forms before reaching the macroscopic phase separation temperature of the binary solvent. Fitting the data to Lorentz model results in a sharp increase in the correlation length when the temperature is approaching the critical point.

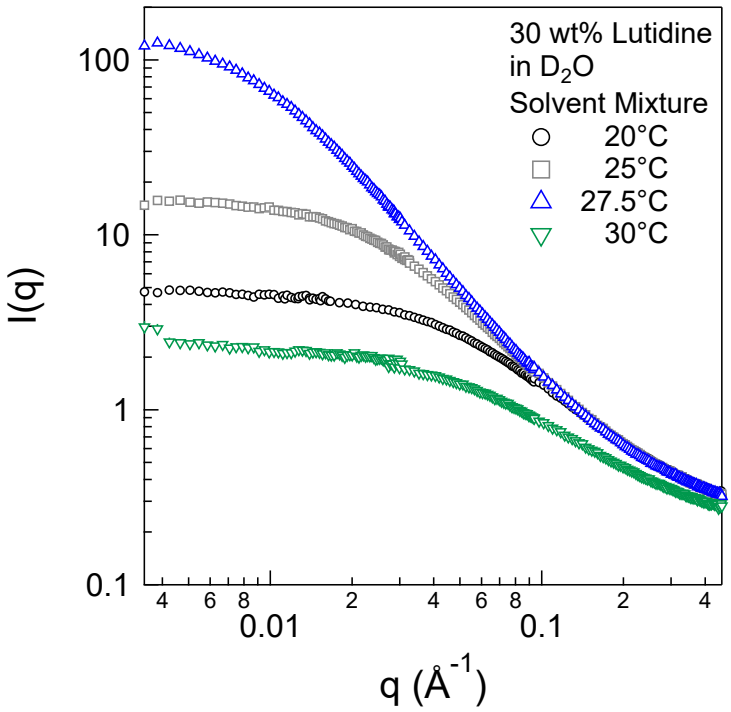

Figure S4 SANS data of 30 wt% 2,6-lutidine/D_2O measured at 20 °C, 25 °C, 27.5 °C and 30 °C.

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