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Solvent structure controlled SeedGel formation investigated using miscible binary solvents[†]

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Recently, a solvent segregation driven gel (SeedGel) has been demonstrated to be a tunable and versatile way to stabilize bicontinuous structures in a binary solvent. Here, the structure properties of the SeedGel prepared with two miscible solvents, 3-methylpyridine (3MP)/water and deuterated 3MP (d-3MP)/water, are systematically investigated using ultra-small angle neutron scattering (USANS), small angle X-ray and neutron scattering (SAXS and SANS). The structures of samples prepared with 3MP/water show similar behavior to one previous SeedGel prepared with lutidine/water. Interestingly, the deuteration of 3MP significantly shifts the gelation temperature of the SeedGel. The results also demonstrate that both components of the binary solvent can be exchanged between the formed two domains of a SeedGel when changing the temperature. Importantly, the binary solvent used for the SeedGel preparation does not have to undergo bulk phase transition as a function of temperature. Our results show that the correlation length due to the density fluctuation of the binary solvent is about the same at the gelation transition temperature for all studied SeedGels prepared with different binary solvents. Thus, this correlation length seems to be a key controlling parameter for SeedGel formation. It is noted that this observation not only holds in binary solvents that show a bulk phase separation but also exists in miscible binary solvents without bulk phase separation. The results here thus open a window to prepare SeedGels with a new set of binary solvents that may have been overlooked before and provide guidance for choosing appropriate miscible binary solvents that can be used to prepare SeedGels.

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Introduction

In the past decades, bicontinuous structures have generated much attention across a wide range of research fields, including energy storage, catalysis, energy saving, memory devices, water treatment, and biomedical applications.^{1–6} In the soft matter community, research related to bicontinuous structures spans

various topics, including polymers, emulsions, and liquid crystals.^{7–9} Their interesting mechanical properties and enhanced mass transport between liquid-filled channels guaranteed a fertile ground for new materials to bloom. The formation of bicontinuous channels in a versatile and tunable manner is extremely important for designing advanced materials.

Since 2005, bicontinuous interfacially jammed emulsion gels (Bijels) have triggered wide-ranging research interest.^{2,10–13} Bijels are composed of binary solvents that phase separate in response to temperature changes and particles that are neutrally wetted to both components of a binary solvent. The gel forms due to the jamming of particles at the liquid–liquid interface when the binary solvent is quenched into the two-phase region. During the phase separation of the binary liquids, the particles remain at the interface to arrest the bicontinuous structures. To prevent the macroscopic phase separation of a sample, a Bijel is often formed by fast quenching into the 2-phase region of a binary solvent. While Bijels are a very interesting class of gel systems, it is also well-known that the preparation of the particle surface is non-trivial, which requires equal preference for both components of a binary solvent. To improve Bijel preparation methods, different approaches are explored to ease the stringent requirements,

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including understanding the particle size effect,¹⁴ implementing particles of different types,¹² changing the shape of particles such as rod-like particles,¹⁵ and adding ion-pairing polymers.¹¹ The phase diagrams of the pure binary solvents are routinely used to guide researchers in selecting the right solvent system and temperature for Bijel formation. The solvent pairs of water/2,6-lutidine,¹⁰ ethanediol–nitromethane,¹³ ethylene carbonate/*p*-xylene,¹² and styrene trimer/polybutene¹⁶ have been studied. All these binary solvents phase separate by changing the temperature (partially miscible).

Recently, a different approach to form bicontinuous structure gels using binary solvents was proposed and demonstrated, and is named a solvent segregation driven gel (SeedGel).^{6,17–19} While Bijel formation relies on the macroscopic phase separation of binary solvents, SeedGel formation is triggered by the phase separation of binary solvents on the nanometer scale before reaching the phase-separation temperature of the bulk solvents. The local phase separation drives the aggregation of nanoparticles. The formation of the gel by the particles, in turn, causes the macroscopic phase separation of the binary solvent commensurate with the bicontinuous channels formed by the particles. Instead of pinning at the interface between two phase-separated liquids as that in Bijel, the particles in the SeedGel are closely packed within one of the solvent domains. The domains exhibit tortuous shapes with micrometer-sized channels. In the gel state, the structures of these bicontinuous channels remain the same despite the temperature change. However, the relative compositions of the two solvents in both domains keep changing due to the exchange of solvent molecules between domains.¹⁸

More interestingly, some SeedGels exhibit structural color, which opens a door to stimuli-responsive materials for controlling the light and heat flow.¹⁸ By changing the temperature, the wavelength of the light passing through SeedGels can be reversibly adjusted due to the aforementioned solvent exchange between domains. For a given solvent system, temperature dictates the wavelength of light that transmits through a SeedGel sample.

So far, the structural tunability and reversibility of SeedGels have been extensively studied in a model binary solvent of water/2,6-lutidine.^{6,17} The dynamics of particles in SeedGels were also investigated. It was found that the relaxation time of particles in the SeedGel is closely related to the mechanical properties of the SeedGel.¹⁹ As SeedGel is a complex system with a wide range of potential applications, exploring different binary solvent pairs is useful for developing a general design guideline for predicting new materials. It can further extend the temperature range of gel formation, making it more versatile to accommodate the requirements of various applications.

In this work, we systematically investigate the structural properties of the SeedGel prepared with two binary solvents, 3-methylpyridine (3MP)/water and deuterated 3MP (d-3MP)/water. The optical properties of the SeedGel prepared using 3MP/water have been briefly mentioned in our prior publication.¹⁸ However, the structural properties and the physical mechanisms of gel formation were not investigated. In sharp

contrast to the partially miscible binary solvents explored in many Bijel and SeedGel studies, there is no bulk macroscopic phase separation at ambient pressure at all temperatures for 3MP/water.^{20–24} While the nanometer solvent phase separation is the key trigger to introduce the attraction between particles for SeedGel formation, all binary solvents used in most previously studied SeedGel systems have a macroscopic phase separation temperature of the bulk solvent not very far from the gel temperature. The formation of the SeedGel in 3MP/water and deuterated 3MP (d-3MP)/water thus helps us further understand the role of a binary solvent in SeedGel preparation. Here, we demonstrate that the correlation length due to the density fluctuation of a binary solvent seems to be a key controlling parameter for SeedGel formation. This thus points to a new direction for discovering new binary solvents for SeedGel formation by working with binary solvents without macroscopic phase separation, which may have been overlooked before.

Experimental

Materials

The silica nanoparticle dispersion (Ludox TM-50, Lot # MKCG0820) was purchased from Sigma Aldrich (St Louis, MO). Hydrogenated solvents, *h*-3-methylpyridine (*h*-3MP) and 2,6-lutidine were ordered from Tokyo Chemical Industry (TCI, Portland, OR). Deuterated solvents, *d*-3-methylpyridine (*d*-3MP) and deuterium oxide were obtained from Cambridge Isotope Laboratories (CIL, Tewksbury, MA). The chemicals were used as received without further purification. Distilled water was used in the preparation of binary solvents.

SeedGel preparation

The preparation of the SeedGel followed the previous work.^{6,17–19} A brief summary is given here. 400 microliters of *h*-3MP (or *d*-3MP) were added to 1 milliliter of Ludox TM™ in a glass vial. It has been determined that the silica nanoparticles in Ludox TM™ are around 27 nm in diameter with 10% size polydispersity.⁶ Similar to the SeedGel formed in 2,6-lutidine/H₂O, a gel forms as soon as 3MP is added to the silica nanoparticle dispersion. Repeated vortexing of the mixture in a capped vial ensured a well-mixed system. The vial was left overnight in a rolling mixer under ambient conditions, which applied a continuous slow shear to the sample. Eventually, a transparent and well-dispersed sample was formed. The SeedGel is induced upon increasing the temperature of the sample. Depending on the temperature, the formed SeedGel can be visibly opaque, which may become transparent by adjusting the temperature. The transparent sample also exhibits a structural color under white light. The detailed characterization and explanations of the optical properties are documented in our recent work.¹⁸

UV-vis spectroscopy

A Thermo Scientific Evolution 201 UV-vis spectrometer (Waltham, MA, US) was used to measure the temperature-dependent optical

transmission spectrum. The samples were sealed in a cuvette with a path length of 1 mm. A Peltier element connected to a thermal bath was used to accurately control the temperature. A thermocouple was placed in the vicinity of the sample and the temperature reading was recorded. For each temperature change, a sample was equilibrated for about 10 min before each measurement.

Small angle neutron scattering (SANS) and ultra-small angle neutron scattering (USANS) measurements

SANS and USANS measurements were conducted at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL, Oak Ridge, TN). The SANS experiments were performed using an extended Q-range SANS diffractometer (EQ-SANS, BL-6).²⁵ The scattering data were stitched together using 1-D profiles recorded at both 4 m and 8 m to achieve a q -range of $0.003 \text{ \AA}^{-1} < q < 0.5 \text{ \AA}^{-1}$. Neutrons with a wavelength range between 2.5 Å and 6.1 Å were selected for measurements at 4 m detector distance and a wavelength range between 10 Å and 13 Å was used for measurements at 8 m detector distance. Banjo cells with a 1 mm path length were used. The scattering background from an empty Banjo cell was recorded and carefully subtracted. Peltier units with an external thermal bath were used to control the temperature of each sample block between 20 °C and 80 °C. The USANS experiments were conducted using the BL-1A beamline at SNS,²⁵ which covers a q -range of $6 \times 10^{-5} \text{ \AA}^{-1} < q < 1 \times 10^{-3} \text{ \AA}^{-1}$. The sample environment allowed the loading of 9 samples simultaneously. Each of the three blocks was able to independently control the temperature of 3 sample cells. Data reduction for SANS followed standard procedures implemented in drtsans.²⁶ Data reduction for USANS also followed standard procedures using the Python scripts developed for the instrument.

Part of the SANS experiments (shown in the ESI†) was performed on the 30 m NGB30 beamline at the NIST Center for Neutron Research (NCNR, Gaithersburg, MD, USA).²⁷ A q -range between 0.001 \AA^{-1} and 0.461 \AA^{-1} , where q is the scattering wave vector, was obtained by stitching data from three detector positions. The temperature was controlled with a precision of $\pm 0.1 \text{ }^\circ\text{C}$ using heating and cooling blocks driven by Peltier. More than 30 minutes is waited to ensure the equilibration of the sample after the temperature change. The scattering data collected at NIST was reduced using the standard Igor (Wavemetrics, Portland, OR) macro.²⁸

Small angle X-ray scattering (SAXS)

SAXS experiments were conducted using an 11-BM (complex materials scattering, CMS) beamline at the National Synchrotron Light Source II (NSLS-II) at the Brookhaven National Laboratory (BNL, Upton, NY). A 3-pole wiggler source was used for X-ray generation. A rectangular beam was defined by slits with a size of 0.2 mm H \times 0.2 mm V. The samples were loaded into Boron-rich capillaries with an outside diameter of 1 mm (Charles Supper Company, Westborough, MA). The capillaries were sealed with epoxy. Multiple samples were loaded on a custom-designed heating stage for measurements at several temperatures from room temperature to 78 °C. The SAXS

signals were collected using a Pilatus 2M detector (Dectris) located at a distance of 5.05 m. The distance was calibrated using silver behenate. The typical exposure time was 10 s and there was a 10 min delay at each temperature to ensure equilibration of the sample.

Results and discussion

Previously, a solvent segregation driven gel (SeedGel) was demonstrated to be stabilized using nanoparticles in a phase-separating binary solvent.^{6,17–19} To form a SeedGel, one of the solvent components has to preferentially wet the nanoparticle surface. A model binary solvent, 2,6-lutidine and water, was used previously with a lower critical solution temperature (LCST) of 34 °C.⁶ As the gel formation is triggered by nanometer aggregates formation, this system forms a SeedGel at about 26 °C, which is 8 °C below the temperature of the critical point of the bulk binary solvent.^{6,17–19} The difference between the gelation temperature and the phase separation temperature of the binary solvent is because SeedGel formation is triggered by the nanometer scale phase separation of the binary solvent, rather than macroscopic phase separation. In contrast, the widely studied bicontinuous interfacially jammed emulsion gel (Bijel) system requires a quench deep into the two-phase region to arrest the bicontinuous structure because macroscopic phase separation of the binary solvent is required in Bijel.^{10,12,13} The regions of Bijel and SeedGel studied in the literature are schematically illustrated in Fig. 1(a). Bijel forms in the two-phase region of the binary solvent, where two components of a binary solvent macroscopically phase separate. In our previous work on SeedGels, we focused on a model system using water and 2,6-lutidine (partially miscible solvent with a macroscopic phase separation temperature). However, a miscible binary solvent, 3MP/water, has recently been found to induce SeedGel formation as schematically illustrated in Fig. 1(b), which broadens the library of solvents that can be potentially used for SeedGels. Here, we systematically investigate the structures and properties of the SeedGels prepared using h-3MP/water and d-3MP/water.

It is well documented that the binary mixture of 3MP and H₂O does not show a macroscopic phase separation at all concentrations at ambient pressure.^{20–24,29} To verify this, optical transmissions are used to determine the phase separation temperature of this binary solvent as the transmitted intensity is expected to reduce near the phase separation temperature.²³ The decrease in light transmission is due to the strong scattering from the large droplets formed near the phase separation of binary solvents. UV-vis spectroscopy measurements in Fig. S1 in the ESI† do not show any reduction in transmittance in h-3MP/H₂O between 20 °C and 90 °C. No visual sign of phase separation is observed within the same temperature range evidenced by the inset photographs of the binary solvent after heating up. Thus, our experiment also confirmed that the binary solvent sample of h-3MP/H₂O does not macroscopically phase separate at the temperature up to at least 90 °C at the ambient pressure.

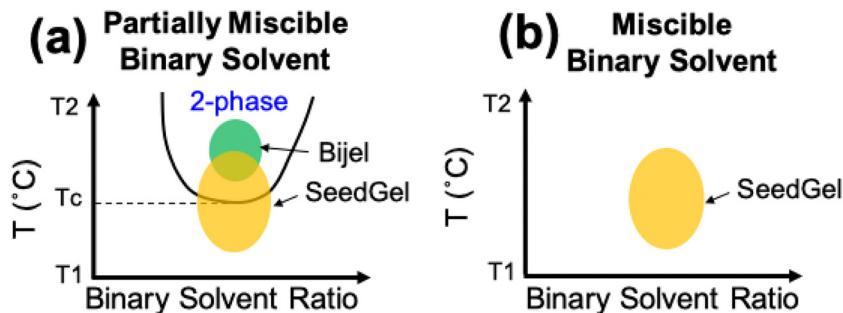


Fig. 1 (a) Schematic phase diagram of both SeedGel and Bijel. SeedGel can be formed close to the critical temperature (T_c) of a binary solvent. Bijel is formed in the 2-phase region above the critical temperature. (b) Schematic drawing shows that SeedGels can also be formed in the binary solvent without T_c .

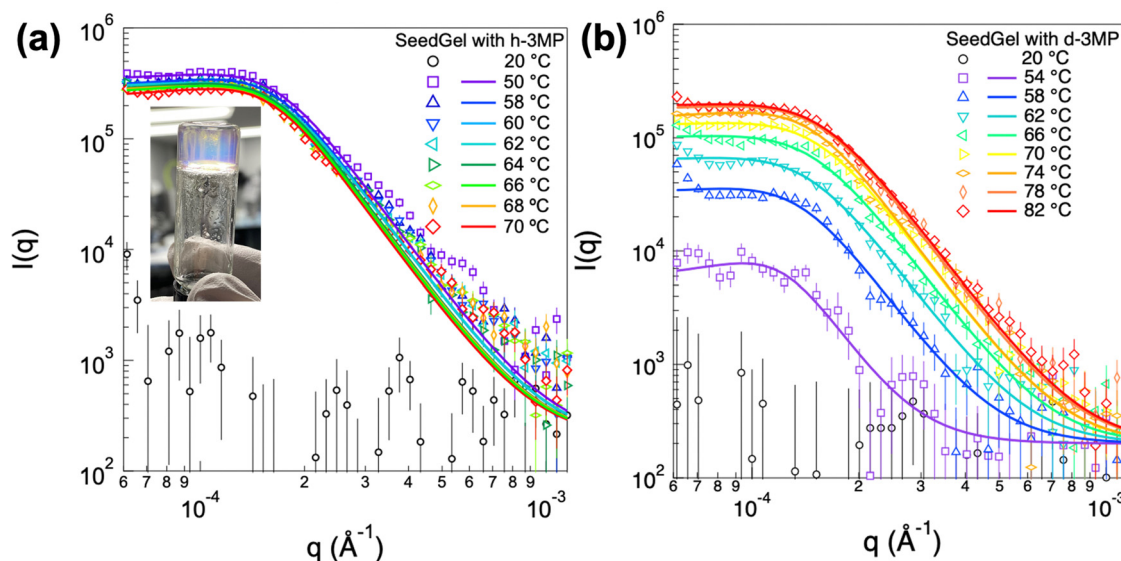


Fig. 2 Smearred USANS profiles of the SeedGel prepared with (a) hydrogenated and (b) deuterated 3-methylpyridine at different temperatures. The experimental data are plotted in open symbols and the fits based on the Teubner–Strey model are plotted in solid lines. The inset photo shows the formed gel in 3MP/H₂O, exhibiting structural colors. The error bars represent one standard deviation and are often smaller than the symbol size.

Fig. 2(a) shows the USANS scattering profiles of the samples prepared with charged silica nanoparticles and hydrogenated 3-methylpyridine (h-3MP)/H₂O. The weak scattering intensity at 20 °C indicates that the sample is liquid with well-dispersed nanoparticles in the binary solvent and no micrometer-sized domains are observed in this q -range. The increase of the scattering intensity at 50 °C indicates the formation of micrometer particle domains and solvent channels, which are similar to the scattering features observed in the SeedGel prepared using 2,6-lutidine/water.^{6,17–19} A hump at $q \approx 1.3 \times 10^{-4} \text{ \AA}^{-1}$ suggests a well-repeated distance between domains. The scattering pattern can be modeled with the Teubner–Strey model, which is usually used to describe bicontinuous structures.^{30–32} The fit results are plotted together with the experiment data in Fig. 2(a). The details of the model are included in the ESI.† The periodicity of the structures is estimated to be around 5 μm (Table 1). By increasing the temperature to 70 °C, the q -position of the hump does not shift, except for a slight decrease in the

intensity. This suggests that the size of the bicontinuous domains remains the same once the SeedGel forms. The intensity decrease is due to the solvent exchange between the bicontinuous domains, which alters the contrast between domains. (The solvent exchange will be discussed in detail later in this paper.) The scattering length densities (SLDs) of silica, water (H₂O), and h-3MP are $3.47 \times 10^{-6} \text{ \AA}^{-2}$, $-0.56 \times 10^{-6} \text{ \AA}^{-2}$, and $1.43 \times 10^{-6} \text{ \AA}^{-2}$, respectively. The solvent exchange causes the enrichment of water in the particle domain, which slightly reduces the averaged scattering length density (SLD) difference between the two domains. As the SLDs of water and h-3MP are relatively close to each other, the scattering intensity due to the solvent exchange is small. Using the binary solvent h-3MP/H₂O greatly expands the temperature range in which the bicontinuous structures are stable. When prepared in 2,6-lutidine/H₂O (a partially miscible solvent), the bicontinuous structures are stable within a relatively small temperature range, spanning only about 5 °C, from 27 °C to

Table 1 The domain size and correlation length extrapolated from Teubner–Strey model fittings of the SeedGel prepared in h-3MP/H₂O and d-3MP/H₂O

h-3MP				d-3MP			
<i>T</i> (°C)	Domain size (μm)	Correlation length (μm)	χ^2	<i>T</i> (°C)	Domain size (μm)	Correlation length (μm)	χ^2
50	4.6 ± 0.03	1.1 ± 0.02	4.8	54	5.7 ± 0.2	1.8 ± 0.3	1.1
58	4.5 ± 0.04	1.1 ± 0.02	3.1	58	5.5 ± 0.1	1.3 ± 0.07	2.8
60	4.6 ± 0.03	1.1 ± 0.02	3.6	62	5.4 ± 0.08	1.2 ± 0.05	2.0
62	4.6 ± 0.03	1.1 ± 0.02	2.4	66	5.3 ± 0.07	1.1 ± 0.03	2.5
64	4.6 ± 0.03	1.2 ± 0.02	4.3	70	5.1 ± 0.05	1.1 ± 0.03	1.9
66	4.6 ± 0.03	1.2 ± 0.02	2.8	74	5.1 ± 0.04	1.2 ± 0.03	2.8
68	4.7 ± 0.03	1.1 ± 0.02	2.3	78	5.0 ± 0.04	1.1 ± 0.02	3.8
70	4.6 ± 0.03	1.1 ± 0.02	3.3	82	5.0 ± 0.05	1.0 ± 0.02	2.0

32 °C.^{6,17} Outside this range, the domains of the SeedGel prepared with 2,6-lutidine/H₂O become unstable due to coarsening of the domains. In sharp contrast, the SeedGel formed in hydrogenated 3MP (h-3MP)/H₂O does not show any discernible domain structure changes for over 20 °C (from about 50 °C to 70 °C). The much wider temperature range is attributed to the fact that there is no macroscopic phase separation in h-3MP/H₂O.

To probe the solvent exchange of the binary solvent in the particle domain and the solvent channel, deuterated 3-methylpyridine (d-3MP) is used in Fig. 2(b) to enhance the contrast between the two components of the binary solvent. The most discernible difference induced by using deuterated solvents is the dramatic change in the scattering intensity at different temperatures. It is attributed to the strong contrast change between the two bicontinuous domains resulting from solvent exchange. The SLDs of d-3MP and H₂O are $5.8 \times 10^{-6} \text{ \AA}^{-2}$ and $-0.56 \times 10^{-6} \text{ \AA}^{-2}$, respectively. Because of the dramatic SLD difference between H₂O and d-3MP, SANS/USANS patterns become very sensitive to any solvent exchange between the particle domains and the solvent channels. The particle and solvent volume fractions of the samples prepared with d-3MP are kept the same as those of hydrogenated 3MP (h-3MP) samples. The structure of the formed micrometer domains/channels at elevated temperatures of the SeedGel prepared with d-3MP/H₂O (Fig. 2(b)) is similar to that of h-3MP/H₂O.

The analysis of the USANS patterns reveals a domain periodicity of about 5 μm (Table 1), which is similar to those formed using h-3MP. The domain size of the SeedGel prepared using d-3MP/H₂O is stable and the bicontinuous structures do not coarsen over a wide range of temperatures from 54 °C to 82 °C. The scattering intensity of the SeedGel with d-3MP/H₂O increases with temperature, an opposite trend to that of the SeedGel prepared with h-3MP/H₂O. The SLD of the particle domain is higher than that of the solvent domain for samples prepared with h-3MP/H₂O. Increasing the temperature of the SeedGel in h-3MP/H₂O increases the water concentration in the particle domain, reducing its SLD. Consequently, the contrast between domains decreases with temperature in the h-3MP/H₂O SeedGel. In the sample with d-3MP/H₂O, the SLD of the particle domain is lower than that of the solvent domain because the SLD of d-3MP is much higher than that of h-3MP

and silica. As the charged particles like water, heating the sample increases the H₂O concentration in the particle domain, decreasing the particle domain's SLD further. Due to the mass balance, the enrichment of water in the particle domain results in the hiking of the d-3MP concentration in the solvent channels, increasing the SLD of the solvent domain. Thus, increasing the temperature increases the difference of SLD between domains, resulting in an intensity increase of one and a half orders of magnitude from 54 °C to 82 °C (Fig. 2(b)). The reverse temperature dependence of the intensity change between the two types of samples prepared with h-3MP/H₂O and d-3MP/H₂O is thus due to the opposite change of the contrast (SLD difference) between domains. The solvent change induced scattering intensity change by using deuterated 3MP unambiguously proves the solvent exchange between the particle domain and the solvent channel. Combined with the contrast-variation experiment we performed in the system using an H₂O/D₂O mixture (contrast-matching) and 2,6-lutidine previously,⁶ the results show that both components of the binary solvent exchange between two domains in response to temperature change.

The dynamic solvent exchange between the particle domain and solvent domain in the gel state affects the temperature-dependent optical properties in some SeedGels,¹⁸ as the wavelength of light passing through a sample is controlled by the temperature-dependent refractive index change of the bicontinuous domains. The refractive indexes of the two bicontinuous domains show different wavelength dependence (different dispersion curves). At a given temperature, the dispersion curves of the two domains only intersect at one wavelength. The refractive indexes mismatch at all other wavelengths. Light at the wavelength with a matched refractive index has the maximum transmission through the sample while others at different wavelengths are significantly attenuated. As the solvent exchanges between the bicontinuous domains with temperature, the refractive indexes of both domains change simultaneously. So does the wavelength of light with the maximum light transmission. This intriguing optical property is also observed with h-3MP/H₂O. The photos in Fig. 3(a) show the sample pictures during a cooling process of a SeedGel prepared with h-3MP/H₂O. The color, due to the scattered light, changes from blue at higher temperatures to yellow. The transmittance during cooling is plotted against the wavelength in Fig. 3(b) within the temperature range that shows color transition for the SeedGel prepared in h-3MP/H₂O. As indicated in the data, peak transmittance is observed at one wavelength for the spectrum at each temperature. The light at the wavelength that is significantly attenuated is scattered by the bicontinuous domains, which contributes to structural color. The yellow color (scattered color) appears when the refractive indexes of the two domains are matched at the short wavelength. Most blue light (short wavelength) is allowed to transmit through the sample, and the longer wavelengths (yellow) are scattered. Increasing the temperature allows the peak wavelength to shift to a longer wavelength, making the sample blue in color (short wavelengths are scattered). This explains

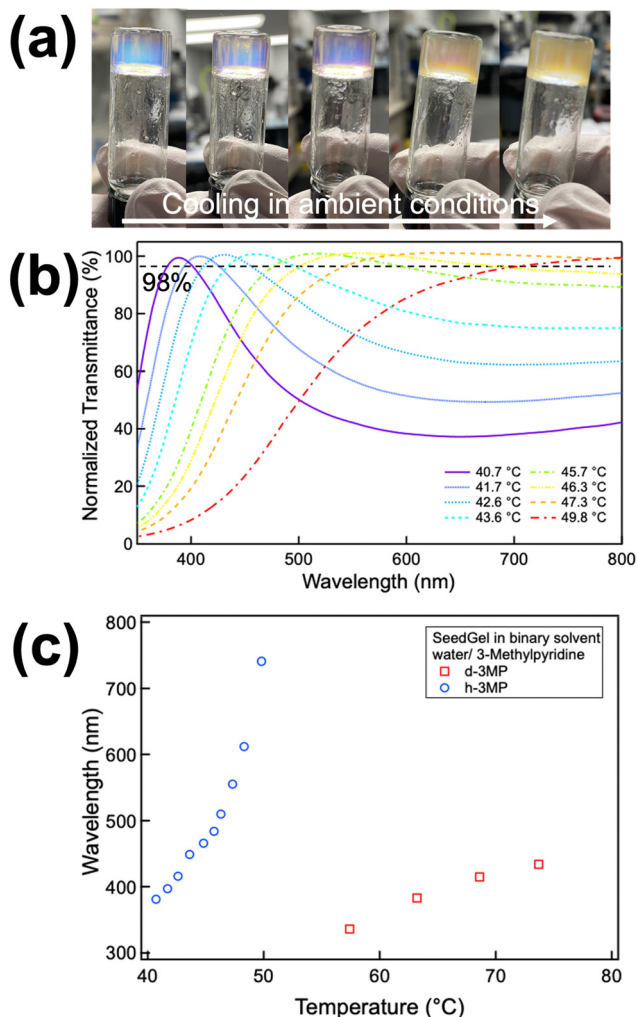


Fig. 3 (a) A series of photos of the SeedGel prepared in h-3MP/H₂O taken during cooling under ambient conditions. (b) Normalized transmittance of the SeedGel prepared in h-3MP/H₂O at different temperatures. The horizontal dashed line indicates 98% of normalized transmittance. (c) The shorter wavelength allows 98% optical transmittance as a function of the measured temperature of the SeedGel prepared with both deuterated and hydrogenated 3-methylpyridine. The volume fraction of 3-methylpyridine in the binary solvent is fixed at 36.4% and the volume fraction of the silica nanoparticles is fixed at 22.7% for both samples.

the color transition in pictures in Fig. 3(a) at different temperatures. To quantitatively compare the wavelength of the transmitted light at varying temperatures, the shortest wavelength that the sample first reaches 98% of the peak transmittance (dashed line in Fig. 3(b)) in a UV-vis measurement is plotted as a function of the temperature in Fig. 3(c). As the path length of the cuvette used is only 1 mm, the peak transmittance is broad at high temperatures. However, the peak of the transmitted light can be greatly sharpened by simply using a cuvette with a longer path length, as demonstrated previously.¹⁸ For the SeedGel prepared with h-3MP/H₂O, the temperature range with adjustable optical transmission is between 40 °C and 50 °C. The onset temperature is also lower than that in d-3MP/H₂O. By replacing h-3MP with its deuterated counterpart (d-3MP),

the temperature of the visible light modulation is significantly increased by about 20 °C to approximately 60 °C. The working temperature change for the SeedGel in d-3MP/H₂O is larger to achieve the same wavelength shift. In other words, the transmittance of the SeedGel in h-3MP/H₂O is more sensitive to temperature change. The isotope effect in the SeedGel provides a general way to tune the temperature range of a SeedGel sample. Even though the isotope effect of water is well known to create an immiscible region in the phase diagram of 3MP/D₂O starting at around 40 °C,²⁴ we did not find a systematic study of the phase diagram of the binary solvent of d-3MP/H₂O in the literature. Experimentally, we have determined that the binary solvent of d-3MP/H₂O does not show macroscopic phase separation within the temperature and concentration range of interest, evidenced by the identical optical transmission over a wide range of temperatures (Fig. S2 in the ESI†). Thus, even though neither the binary solvent of h-3MP/H₂O nor d-3MP/H₂O shows macroscopic phase separation, they are still able to be used to prepare SeedGels. The SeedGels formed in this way also exhibit dynamically tunable optical transmission. The formation of the SeedGel and its associated optical properties in a miscible binary solvent 3MP/H₂O indicates that SeedGel formation does not require the macroscopic phase separation temperature by the solvent themselves. This property expands the types of solvent systems that can be used for SeedGel formation. The results also demonstrate that isotopic substitution can be used to change the gelation/color transition temperature of the SeedGel without searching for new solvent pairs.

To investigate the structures at the nanometer scale during SeedGel formation, small angle X-ray scattering (SAXS) experiments were performed on SeedGels at different temperatures (Fig. 4). Fig. 4(a) shows the results of the SeedGel in h-3MP/H₂O. The peak at around 0.023 Å⁻¹ is related to the average distance between silica nanoparticles. At temperatures below 36 °C, silica nanoparticles are relatively uniformly dispersed in 3MP/H₂O. The SAXS pattern shows a broad hump at around 0.019 Å⁻¹, indicating that the sample is in the liquid state. Beginning at 36 °C, the peak becomes sharper and gradually shifts to higher-*q* positions. This is due to the SeedGel formation with bicontinuous domains. The temperature increase drives the phase separation of the binary solvent at the surface of particles. At elevated temperatures, water is enriched on the particle surface, which attracts particles together to form aggregates. The random-sized aggregates explain the broad hump in the scattering profiles below 0.02 Å⁻¹ between 36 °C and 40 °C. As the sample is further heated, the water and particles aggregate together to minimize contact with 3MP. So, water becomes more and more enriched in the aggregates as temperatures increase. Eventually, bicontinuous particle domains percolate throughout the sample to form a SeedGel, with water being the main solvent in the particle domain and the silica nanoparticles being tightly confined in the particle domain. The narrow distribution of the particle–particle distance results in a sharper peak in SAXS patterns, and a closer packing between particles leads to the peak shift to a high-*q*

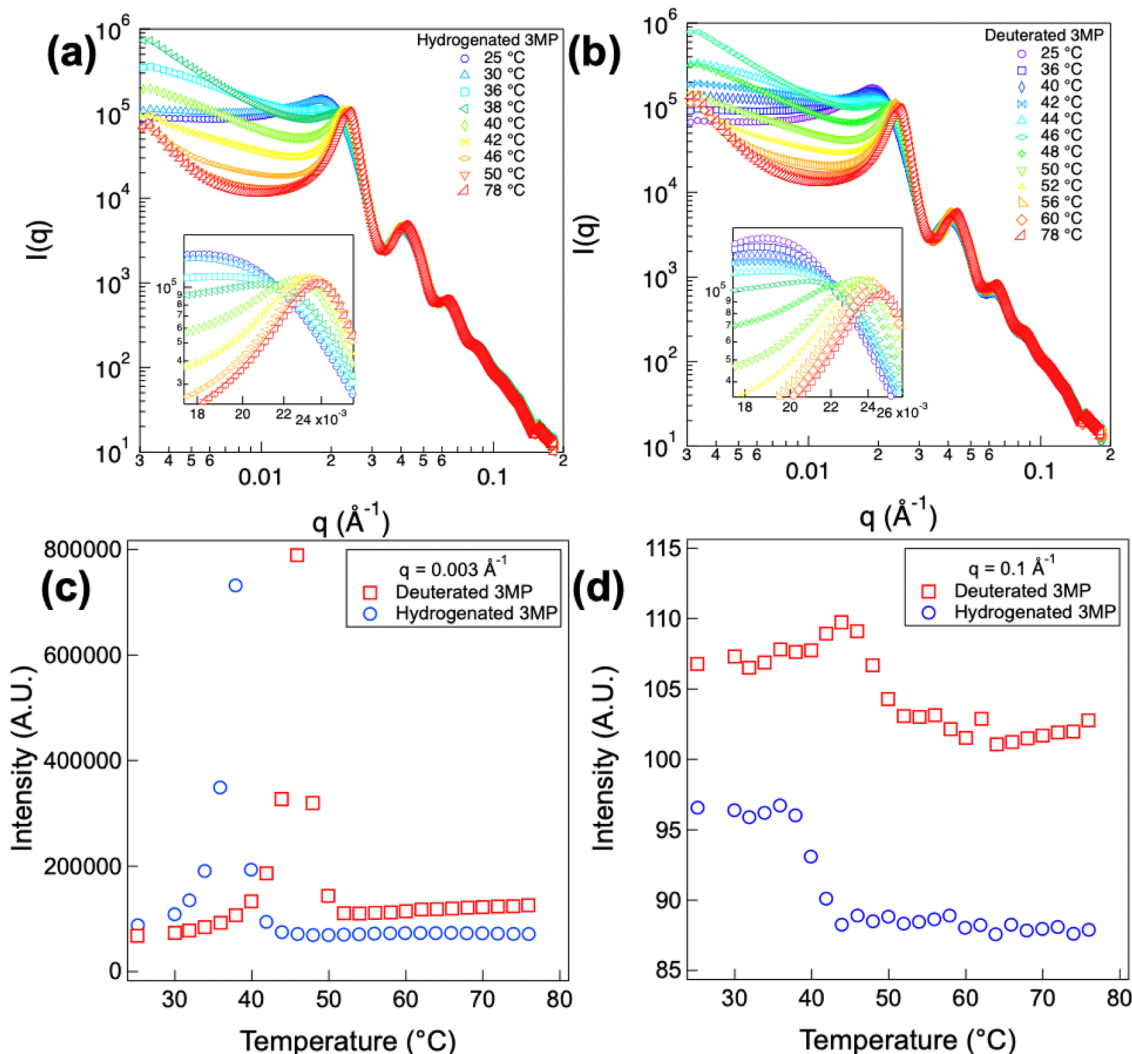


Fig. 4 SAXS results of the SeedGel prepared with (a) hydrogenated and (b) deuterated 3-methylpyridine measured at different temperatures. The comparison of the intensity between the two samples as a function of temperature at (c) 0.01 \AA^{-1} and (d) 0.1 \AA^{-1} .

position, consistent with a previous study.⁶ The peak position shifts to around 0.0239 \AA^{-1} at temperatures above $40 \text{ }^\circ\text{C}$. The same trend is observed in the SeedGel prepared in d-3MP/ H_2O (Fig. 4(b)), but with a drastically different transition temperature. The shift of the peak position to a higher- q value does not occur until above $50 \text{ }^\circ\text{C}$, denoting a higher SeedGel formation temperature. The deuteration of one of the solvent components greatly increases the gelation temperature by more than $10 \text{ }^\circ\text{C}$. The difference in the SeedGel formation temperature is consistent with a much higher color transition temperature shown in Fig. 3. Implementing d-3MP also exhibits tighter particle packing when compared to the SeedGel utilizing h-3MP. In the gel state, the q -position shifts to a higher- q value (0.0248 \AA^{-1}), suggesting a reduced particle-particle distance for the d-3MP SeedGel.

To better analyze the relationship between the temperature and the structural change of the SeedGel, the intensities at $q = 0.003 \text{ \AA}^{-1}$ and $q = 0.1 \text{ \AA}^{-1}$ are plotted as a function of temperature for the SeedGel in Fig. 4(c) and (d), respectively.

By increasing the temperature from $25 \text{ }^\circ\text{C}$, the initial intensity increase at a low- q value (below 0.01 \AA^{-1}) before the SeedGel formation is due to the formation of aggregates. A substantial change in the SAXS scattering profiles is observed during the gel formation. In Fig. 4(c), the reduction of the intensity after reaching its maximum value is due to the formation of micrometer bicontinuous domains, shifting the scattering profile to a low- q value outside the q -range probed by SAXS. The difference in the transition temperature between the hydrogenated and the deuterated samples is about $10 \text{ }^\circ\text{C}$ based on the SAXS results, which is consistent with the UV-vis results shown in Fig. 3. The intensity change at high- q (0.1 \AA^{-1}) is also analyzed in Fig. 4(d). The scattering intensity difference at this q -range is mainly related to the solvent composition change in the particle domain since it is mainly due to the change of the scattering length density difference between particles and solvent in the particle domain. By increasing the temperature, the intensities of both samples first increase slightly and then suddenly decrease. The sharp decrease of the intensity at about $39 \text{ }^\circ\text{C}$

for the 3MP/H₂O system indicates the solvent phase transition temperature. For the h-3MP/H₂O and d-3MP/H₂O systems, the transition temperature differs by about 10 °C. For X-rays, the scattering length density (SLD) of H₂O is higher than that of 3MP. The SLD of silica is larger than both 3MP and water. A higher H₂O concentration near the particles results in a lower contrast between particles and the surrounding solvent, thus reducing the scattering intensity. Once the SeedGel forms, the scattering curves remain mostly unchanged as a function of temperature (Fig. 4(a) and (c)). Note that there are still small amounts of solvent exchanges between the particle domains and the fluid domains. Even though the exchange is large enough to change the optical properties, it is so small that its impact on the SAXS patterns is very minimal once the SeedGel

forms. This is consistent with the USANS results (Fig. 2(a) and (b)), where the high-*q* data are similar to each other at different temperatures above 50 °C in the gel state. In addition, the data around the high-*q* peak is fitted using the Hayter–Penfold method, from which the volume fraction of particles in the particle domain is estimated to be around 41%. As the particles are tightly packed within the particle domain, the *S*(0) value is fairly small. The fitting results can be found in Fig. S3(a) and (b) in the ESI.†³³

To further understand the controlling factor of the binary solvent that drives the formation of the SeedGel, small angle neutron scattering (SANS) measurements were used to study the properties of pure binary solvents for h-3MP/H₂O and d-3MP/H₂O at different temperatures. Despite h-3MP and

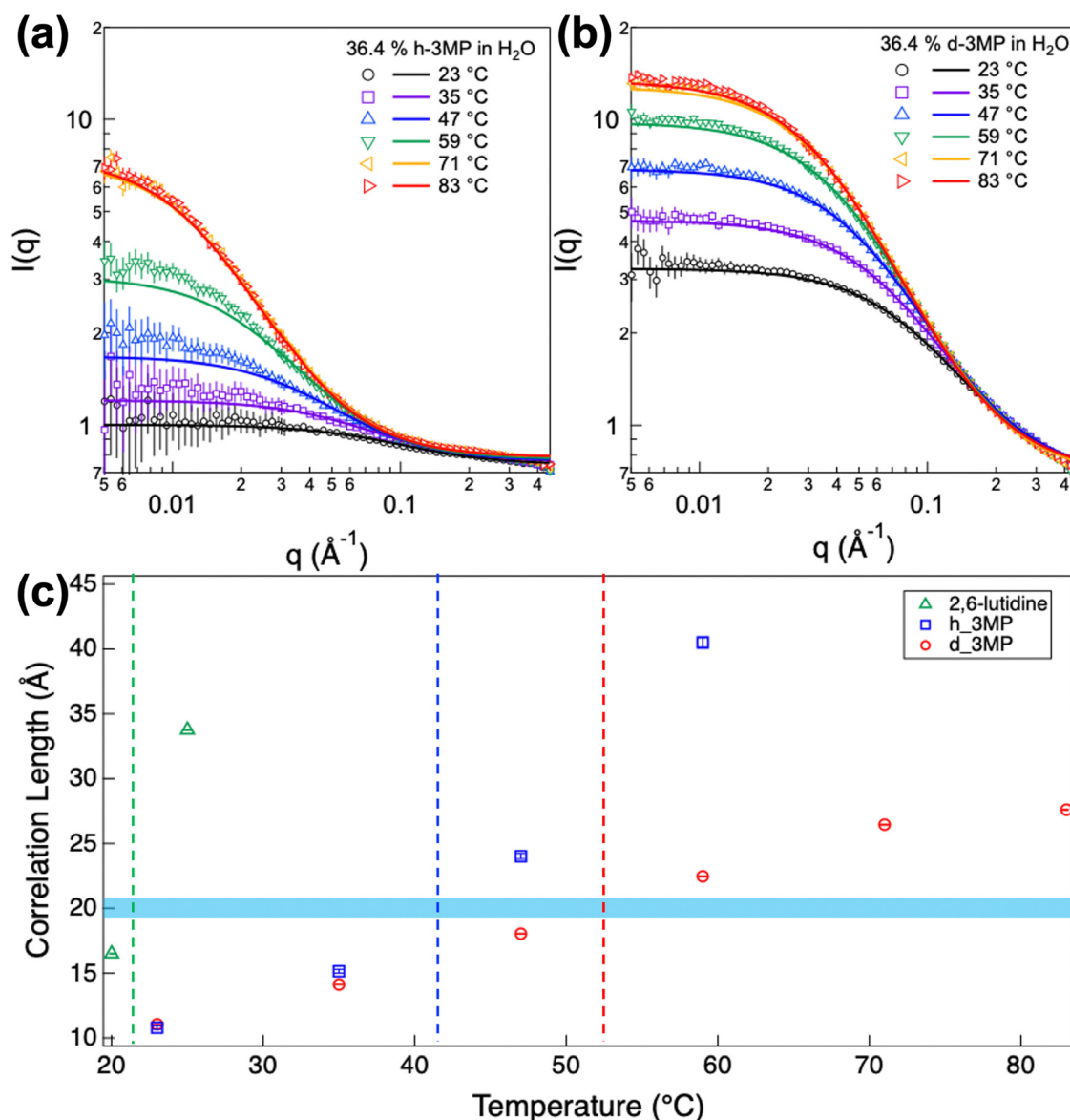


Fig. 5 SANS profiles of the binary solvent of (a) hydrogenated 3-methylpyridine/H₂O and (b) deuterated 3-methylpyridine/H₂O at different temperatures. (c) The correlation length of 2,6-lutidine/D₂O, h-3MP/H₂O, and d-3MP/H₂O extrapolated from the Lorentz model at different temperatures. The green, blue, and red dashed lines represent the gelation temperatures of the SeedGels prepared in binary solvents 2,6-lutidine/H₂O, h-3MP/H₂O, and d-3MP/H₂O, respectively. The blue stripe represents a general guideline that connects the critical correlation length in the three binary solvents together.

H₂O being fully miscible, SANS patterns show some structures at the nanometer scale with increasing temperature (Fig. 5(a)). Similar SANS patterns are also observed for d-3MP/H₂O (Fig. 5(b)). A Lorentz model is used to fit the scattering patterns of the binary solvent to obtain quantitative information. The details of the Lorentz model are shown in the ESI.† The fit results are plotted with the experimental data in Fig. 5(a) and (b).

The correlation length is obtained from the Lorentz model for binary solvents of both h-3MP/H₂O and d-3MP/H₂O. They are plotted as a function of temperature in Fig. 5(c). In general, increasing the temperature increases the correlation length, indicating the formation of nanodomains of solvent molecules. For h-3MP/H₂O, the correlation length of the bulk solvent is about 20 Å at about 40 °C, which is the gelation transition temperature of the SeedGel prepared with h-3MP/H₂O. Interestingly, for the SeedGel prepared with d-3MP/H₂O, the correlation length of the bulk solvent for d-3MP/H₂O is also around 20 Å at the gelation temperature of the SeedGel, which is around 50 °C. Thus, for the same silica particle systems, it seems that the controlling factor of the SeedGel formation is the correlation length of the bulk binary solvent. The correlation length of 2,6-lutidine and D₂O obtained from Lorentz model fitting is also studied and included in Fig. 5(c). The SANS results of the binary solvents 2,6-lutidine/D₂O are plotted in Fig. S4 in the ESI.† Note that in order to make a fair comparison between the SeedGels formed among the three systems, the same batch of silica nanoparticles was used. The vertical dashed lines in Fig. 5(c) are the SeedGel gelation temperatures when prepared in the three binary solvents. Again, a SeedGel forms when the correlation length of the binary solvent reaches around 20 Å. Therefore, this could be an important design guideline when choosing a binary solvent to prepare SeedGels from the silica particles used in this paper.

It has been previously observed that water-rich layers are adsorbed on the surface of charged silica nanoparticles.^{34,35} The water condensation induced by solvent fluctuations acts as an attractive force to assemble nanoparticles in a 2,6-lutidine/water mixture.^{34,35} The formation of the SeedGel is driven by this attractive force in the binary solvent. Even though no critical temperature exists in the mixtures of h-3MP/H₂O and d-3MP/H₂O for the temperature up to about 100 °C,²³ there is nanometer structure formation in 3MP/H₂O. The density fluctuation of around 2 nanometers would be enough to induce the formation of a SeedGel. This critical correlation length is hypothesized to be related to the particle surface property and size. The correlation length is linked to the water absorption thickness, which is determined by the solvent property. Due to the aforementioned attractive force, the absorbed liquid layer bridges the particles together to form aggregates. As a result, the further phase separation of the binary solvents is facilitated by the pores formed by the surrounding nanoparticles. The size of the pore, which is determined by the size of the nanoparticles, is closely related to the phase-separation of the solvents, and thus, the formation of the SeedGel. It is hypothesized that the gelation temperature of the SeedGel can

be tuned by either the surface property or the particle size, which needs systematic investigations in the future.

Conclusions

The microscopic structures of the SeedGels prepared with h-3MP/H₂O and d-3MP/H₂O are systematically investigated here. Different from all the previous binary solvents used for the preparation of SeedGels, the binary solvents studied in this paper do not show phase separation macroscopically for temperatures up to about 100 °C. Yet, nanoparticles dispersed in these two binary solvents can also form SeedGels. This distinguishes SeedGels from Bijels, as macroscopic phase separation of the binary solvent is not a requirement for SeedGels. It also broadens the solvent systems that can be used for SeedGel formation.

While the domain structures maintain the same size at different temperatures in the formed SeedGel, contrast variation USANS experiments reveal the solvent exchange of the organic component of the binary solvent between bicontinuous domains. Combined with previous results, the present work clearly demonstrates that both components of the binary solvent can be exchanged between the two domains of the SeedGel when changing the sample temperature. Using deuterated 3MP can significantly shift the gelation temperature of SeedGel formation. A close relationship between the correlation lengths of the density fluctuation of binary solvents and the SeedGel formation temperature is observed. It is found that a SeedGel is formed when the correlation length in the binary solvent reaches around 2 nm for the charged silica particles used in these studies. This correlation length is likely a function of the particle properties that need to be investigated in future studies.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

Y. X. and Y. L. are inventors on a PCT international patent application related to this work filed by the University of Delaware (no. PCT/US2021/070989 filed [July 27th, 2021]).

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