

2.1 – Introduction

During the sol-gel transformation, a system's physical properties transition from being liquid-like to solid-like. Notably, the viscosity and the shear modulus increase significantly during gelation, and have been used as a way to identify the gelation point.^{1,2} The measurement of these properties often requires application of some physical force or stress onto the system, which can potentially be disruptive to a mechanically fragile polymer network. The ability to measure the progression toward the gelation point in a non-invasive manner is ideal, as it is unlikely to influence the observed gelation time. Feng *et al* demonstrated that the shear modulus is linearly related to the nuclear magnetic resonance (NMR) relaxation times of unbound species in peptide sol-gel systems.³ This study focused on the free monomeric units in particular because their signal was detectable even through the sol-gel transition. It is not unreasonable, then, to extend this finding to the solvent phase of a sol-gel system, as it is still measurable beyond the gelation point.

The work described herein seeks to non-invasively probe the physical changes that cyanogel mixtures undergo during the sol-gel transformation. Water, the solvent that becomes the fluid phase of the gel, can be examined by *in situ* spectroscopy to provide a picture of the changes the system is undergoing. In particular, this study focuses on the use of NMR and attenuated total reflectance infrared spectroscopy (ATR-IR) to characterize relaxational changes, differences in diffusion, and changes in the intermolecular interactions of the water.

2.1.1 – Relaxation in Nuclear Magnetic Resonance Spectroscopy

In NMR spectroscopy, an external magnetic field is used to align nuclear spins whose individual angular magnetic moments precess with what is known as the Larmor frequency (ν_0).

Nuclei are excited when a radio frequency (RF) signal is applied transverse to the external magnetic field, along which the z axis conventionally defined. In this excited state, the net nuclear magnetic moment is not aligned with the field. After the RF pulse, the magnetic moment continues to precess about the z axis, inducing an oscillating voltage in the detector coil of the instrument if the magnetization vector is nonzero in the transverse (xy) plane. This oscillating signal, known as free induction decay (FID), dampens over time as the nuclear spins return to their equilibrium distribution in a process known as relaxation. NMR relaxation falls into two categories: spin-lattice relaxation and spin-spin relaxation.

Spin-lattice relaxation (T_1) is associated with the loss of signal intensity. As the name implies, this relaxation is due to energy transfer between the excited nuclei and the surrounding chemical “lattice”, which can be considered any neighboring atoms, even if the proximity is transient. This energy transfer allows the nucleus to return to its thermal equilibrium state. The relaxation takes place in the direction of the applied external magnetic field (M_z), and is sometimes referred to as longitudinal relaxation. For protons, T_1 typically does not vary much in different bonding situations. However, T_1 is highly dependent on the strength of the magnetic field and on the presence of paramagnetic species within the system.

One type of experiment that is commonly used to measure spin-lattice relaxation is inversion recovery.⁴ As seen in Figure 2.1, inversion recovery experiments start with a 180° pulse, to invert the nuclear spins. After a delay, τ , a second pulse is applied at 90° , creating measurable transverse magnetization. By varying τ , different signals are produced. T_1 can then be extracted by fitting the inversion recovery data to equation 2.1, wherein M_0 corresponds to the equilibrium magnetization vector and M_z corresponds to the z component of the magnetization vector after a given delay, τ .

be fit to the equation

$$I = I_0 e^{-D\gamma^2 g^2 \delta^2 (\Delta - \frac{\delta}{3})} \quad \text{(Equation 2.4)}$$

where I is the measured intensity, I_0 is the unattenuated reference intensity, D is the diffusion coefficient, γ is the gyromagnetic ratio of the nucleus, g is the applied gradient strength, δ is the length of the gradient, and Δ is the diffusion time. Because many of these conditions are held constant, diffusion coefficients can be obtained from this fit.

2.1.3 – High Resolution Magic Angle Spinning

The use of standard NMR techniques to study solids is made difficult due to the intermolecular interactions between neighboring nuclei. These interactions – dipole-dipole interactions, chemical shift anisotropy, and quadrupolar coupling – often lead to very broad features in the spectrum. However, by spinning the sample at the “magic angle” ($\Theta_m = 54.7^\circ$) with respect to the applied magnetic field, the spectra resolve into identifiable peaks. At this angle the nuclear dipole-dipole interactions of a sample average to zero and the chemical shift anisotropy averages to a non-zero value. The quadrupolar coupling is only partially averaged out, leading to distinct spinning sidebands for each peak in the spectrum. By adding a deuterium lock channel to this technique, increased resolution is possible in condensed matter. Addition of a magnetic field gradient along the magic angle rotational axis further improves the spectral resolution, such that the spectra resemble those collected by liquid-phase NMR.¹¹ This technique, referred to as high resolution-magic angle spinning (HR-MAS) is ideal not only for solids, but for viscous liquids, rigid polymers, and gels. A diagram of the HR-MAS probe is seen below in Figure 2.5.

H₂O/D₂O mixture with 5% chloroform by volume as a non-reactive internal probe. Four types of measurements were made on the samples. First, ¹H NMR was collected to examine the chemical environments of the H₂O and the CHCl₃. This was followed by an inversion recovery experiment to determine the spin-lattice relaxation time (T₁) of each proton environment present. Next, a spin-echo experiment was used to determine the spin-spin relaxation time (T₂) of each environment. Finally, diffusion-ordered spectroscopy (DOSY) was used to determine the diffusion coefficients of the proton-containing species in the mixture. These experiments were repeated sequentially during the polymerization process (¹H, T₁, T₂, DOSY), such that the timing between two experiments of the same type was 50 minutes. Under standard conditions, these mixtures gel in several days or up to a week.

A 30:15 mM mixture of PdCl₄²⁻ and Co(CN)₆³⁻ (PdCo) was examined on the same instrument at a spin rate of 600 Hz. Under standard conditions, PdCo gels are observed to form in a matter of minutes to hours. Due to the lower gelation time of PdCo compared to PtRu and PtFe, only proton and DOSY experiments were run, with intervals lasting 15 minutes between experiments. The internal standard used for the PdCo sample was dichloromethane, which is also expected to be unreactive.

Control proton and DOSY experiments were performed on two control mixtures of H₂O/D₂O with 5% of the unreactive probe by volume (chloroform in one sample, dichloromethane in the other). These controls yielded a conversion constant so that absolute diffusion coefficients could be calculated.

2.2.3 – ¹H NMR Experiments

Solution-phase ¹H NMR is the most commonly used NMR technique. For all samples

considered in this work, ^1H NMR was used to observe changes in spin-lattice and spin-spin relaxations of the water and internal probes that arise due to polymerization and gelation. Samples were prepared in a 60/40 mixture of H_2O and D_2O , providing both a lock for the deuterium channel and a water signal that could be monitored for changes in peak height and width. An internal standard of chloroform (5% by volume) was used to ensure that the observed changes were due to relaxation and not changes to the chemical environment of the water. Samples were mixed directly in a 5 mm NMR tube, and spectra were collected on a Bruker AVANCE III with a 500 MHz magnet.

2.2.4 – ATR-IR Experiments

Gelation mixtures of 30 mM PdCl_4^{2-} and 15 mM $\text{Co}(\text{CN})_6^{3-}$ were examined by attenuated total reflectance-infrared spectroscopy (ATR-IR). These gelation mixtures contained either 100% H_2O or 55% D_2O /45% H_2O as the solvent to provide insight into the behavior of water during gelation. These experiments were performed on a Thermo Electron Nicolet 6700 FTIR spectrometer with a ZnSe ATR element. A custom-made Teflon cell fitted with an o-ring was used to confine the gelation mixture to a cylinder with a diameter of 16 mm on the ATR crystal, as can be seen in Figure 2.6. Prior to each experiment, a background was collected of the appropriate solvent. The experimental samples were then prepared externally, and 400 μL of the mixture was transferred to the cell for spectral analysis. Spectra were collected every 5 minutes until the sample gelled.

termination of the experiment. The evolution of the PtFe system over time confirms that there are physical changes in the system, despite the fact that the gel never forms. The maximum T_1 and minimum T_2 observed around the 40 hour mark suggests that the water exhibits its most clustered behavior at this point, with the correlation time decreasing again afterwards. It is possible that at 40 hours, the oligomeric species within the mixture reached a critical size, beyond which the structure could not be preserved given the rate of rotation of the sample. If this is the case, it is likely that some of the water had been confined within the polymer cluster, increasing the average cluster behavior of the water. Upon the fracture of the polymer backbone, this water would be released, returning to a less clustered behavior. An alternative explanation comes back to the idea of centrifugal force creating a concentration gradient of the oligomeric components. It is possible that over time the oligomeric clusters were compressing some of the fluid along the edges of the sample insert. However, given the higher mass of the oligomeric clusters, particularly as they continue to grow, the forces driving them outwards would be higher than those of water, eventually pushing the water towards the center of the mixture. This counter force driving the water toward the rotational axis would lessen the cluster behavior of the water, again showing this decrease in spin-lattice relaxation and increase in spin-spin relaxation.

2.5.2 – Indirect Measurements via ^1H NMR

The inverse relationship between T_2 and FWHM can be exploited to indirectly measure T_2 from a simple solution-phase ^1H NMR experiment. This is particularly useful for situations in which gelation occurs too quickly to carry out several CPMG experiments, and does not require deviation from ambient conditions. Figure 2.10 shows the change over time in T_2 for water

The diffusion coefficients measured in the PdCo system appear to be more than a full order of magnitude higher than those measured in the PtFe system. This effect may be related to the difference in spin rates, with PdCo at only 600 Hz while PtFe was rotated at 5000 Hz, or to the difference between the compositions of the two gels. Further experiments on the two gelation mixtures across several spin rates would be necessary to determine the actual cause of this discrepancy.

2.7 – ATR-IR Studies of the Hydrogen Bonding Environment of Water During Gelation

During the sol-gel transition, systems go from having liquid-like to solid-like rheological properties. This study uses ATR-IR spectroscopy to investigate if the chemical environment of the gel solvent also reflects this liquid-like to solid-like transformation. Water is able to participate in hydrogen bonding at all three atoms within the molecule, leading to a local tetrahedral geometry in the solid state and an average tetrahedral arrangement in the liquid state. The key difference between these two arrangements is the energy of the molecular vibrations compared to the strength of the hydrogen bonding interaction. In infrared spectroscopy, this difference presents itself as a red shift and sharpening of the features associated with the symmetric (ν_1) and asymmetric (ν_3) stretching modes as the water freezes.¹⁵ This red shift stems from the reduced force constant of the oscillator and the enhanced anharmonicity of the vibrational potential. The bending mode (ν_2) is not affected by these changes and therefore does not shift to reflect the extent of hydrogen bonding.

The effects of hydrogen bonding can be probed by comparing protiated spectra to deuterated spectra. Hydrogen bonding is stronger for ^1H than ^2H , and the difference in mass between the two isotopes leads to significant differences in the observed vibrational frequencies.

To examine the hydrogen bonding environment during cyanogel formation, spectra were collected for a 30/15 mM mixture of PdCo in pure H₂O over the course of 90 minutes, at which point the gel was formed. The water regions of these spectra are shown in Figure 2.15. It is expected that for a system progressing towards solid-like properties, a red shift would be observed, but the data suggests the opposite is occurring. Initially, a slight red shift is observed for the feature centered around 3430 cm⁻¹. Over time, the intensity of this feature decreases, suggesting that the behavioral deviation from the liquid H₂O background is lessened. This feature is likely attributed to the interaction between the nitrogen lone pair on terminal cyanide ligands and hydrogen from water and HOD, which is expected to decrease as cyanide bridges form. This assignment is in agreement with early studies on hydrogen bonding to nitriles and the spectrum of the hexacyanocobaltate(III) precursor solution.¹⁶

More intriguing is the increasingly negative feature centered around 3150 cm⁻¹. This feature suggests that the hydrogen bonding in the PdCo mixture is less than that of pure water, and that the hydrogen bonding interactions continue to weaken over the course of the gelation. The appearance of a third feature centered around 3615 cm⁻¹ seems to suggest the presence of O-H stretches or group stretching modes that do not participate in hydrogen bonding at all.

The plot for the bending mode region employs a small vertical offset for each spectrum so that the spectral shape is more obvious. The features found between 1500 and 1600 cm⁻¹ are attributed to water that has ligated to the Pd center, as confirmed by comparison with a spectrum of the precursor solution backgrounded with water. The single feature at 1630 cm⁻¹ does not show any appreciable change over time, consistent with our expectation for the bending mode of free water.

The results of these IR studies suggest that the hydrogen bonding environment of water is decreased as a cyanogel mixture undergoes the sol-gel transformation. This goes directly against the hypothesis that the chemical environment of the water would begin to resemble water in its solid state as the rheological properties begin to resemble those of solids. This result likely arises due to the largely ionic nature of the system being studied. The anionic polymer, the alkali counteranions, and the free chloride ions (which are expected to increase in concentration over time) likely perturb the hydrogen bonding environment.^{17,18} By using the solvent (H₂O or H₂O/D₂O) as the background prior to these experiments, this method is able to probe minor changes within the system. However, as can be seen from the backgrounding inconsistencies in the H₂O/D₂O system shown, this backgrounding is imperfect and contributes uncertainty to the results of the experiment. It is suggested that further experiments are carried out to investigate the implied result. Continued experiments by ATR-IR with a variety of added salts may provide insight into the electrostatic effects. Raman spectroscopy is also an appealing technique to continue these studies.

2.8 - Conclusions

The intent of these studies was to use non-disruptive techniques to examine the fluid phase of the sol-gel system leading up to and slightly beyond the gelation point. To this end, HR-MAS proved to be inadequate, as the high rate of spinning was observed to slow or completely stall gelation. Magnetic field inhomogeneities and rotation-rate dependence of diffusion measurements suggest that this effect is due to high centrifugal forces that drive the heavier oligomeric material away from the axis of rotation. This, in turn, causes a concentration gradient wherein the polymer is unable to extend across the container until the experiment is stopped.

2.9 – References

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