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Gelation of Xanthan by Trivalent Chromic Ions Monitored by ^1H NMR Relaxation: A Preliminary Study

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Gel formation of xanthan by trivalent chromic ions is investigated within the ^1H NMR relaxation time framework. To our knowledge such an approach has not previously been discussed in the literature, and we found it appropriate to consider this method in some detail. In particular, this NMR technique seems to provide significant information regarding the kinetics of polymer–chromium ion gel formation during the induction period. Moreover, the work presented in this paper suggests that NMR and dynamic mechanical analyses (using oscillatory rheological testing) produce complementary information with respect to such processes.

Introduction

Kinetic studies related to the formation of chromium(III)–polymer gels have been the subject of extensive studies in recent years. The use of high-viscosity polymeric fluids and gels for water flow control in oil reservoirs is well established, with the primary application in enhanced oil recovery, i.e. permeability modification and zone blocking. Different rheological techniques^{1–3} have been applied in order to explore and further understand the kinetics and the reaction mechanisms involved in gel formation processes of polymer–metal ion systems. Also ^{13}C NMR spectroscopy⁴ and UV spectroscopy⁵ have been utilized with this same objective in mind.

The addition of small amounts of paramagnetic salts to pure water has a marked effect on the nuclear spin relaxation rates of water protons as measured by ^1H NMR spectroscopy⁶ and was first considered theoretically by Bloembergen, Purcell, and Pound.⁷ These effects make nuclear magnetic resonance spectroscopy a powerful analytical tool in studying redox, complex formation, and precipitation reaction and even reaction kinetics—in which paramagnetic ions participate—if the overall reaction is accompanied by a change in the effective magnetic moment or a change in the concentration of paramagnetic species.^{8,9} For water protons in aqueous solutions containing paramagnetic ions, the interaction between the electronic spin of the paramagnetic ion and the spins of the neighboring protons is about 1000 times more effective than the corresponding spin–spin interaction between neighboring water protons (dipole–dipole coupling).

Formation of polymer–paramagnetic ion gels should therefore, in theory, be suitable processes for investigation by ^1H NMR spectroscopy. Moreover, it was found advantageous to follow the gelation process by dynamic mechanical analysis using an oscillatory rheological test. Actually, the two experimental techniques are shown to give complementary information. To our knowledge such an NMR study has not been reported previously so we found it pertinent to present some preliminary results obtained on a xanthan–chromium(III) system. A more detailed and comprehensive work on this system is in progress.

Theory

Rheology. Dynamic mechanical analysis using an oscillatory rheological test is already a well-established method applied in the study of gel formation processes.^{1–3} Only a brief outline of the technique will therefore be given. For further details, see for instance ref 1.

The property of interest to this work is the storage modulus G' which, according to rubber elasticity theory,¹⁰ is written

$$G' = G'_{\text{en}} + G'_j \quad (1)$$

where G'_{en} describes the initial polymer–polymer entanglement

and G'_j reflects the junction density or the number of polymer–metal–polymer cross-links. The latter parameter is of particular concern in this study.

NMR Spectroscopy. In addition to the paramagnetic contribution to the spin–spin relaxation rate ($1/T_2$) and the spin–lattice relaxation rate ($1/T_1$) of the solvent water protons, Bloembergen et al.⁷ have shown, both theoretically and experimentally, that the viscosity of the solution also influences the relaxation rate, as indicated by eq 2a, where T_i is the relaxation time of the water

$$1/\eta T_i = (K_i/kT)\mu_{\text{eff}}^2 C \quad i = 1, 2 \quad (2a)$$

protons, μ_{eff} the effective magnetic moment of the paramagnetic ion, kT the Boltzmann energy, and C the concentration of paramagnetic ions in the solution of viscosity η . K_i is a constant dependent on the proton–paramagnetic ion interaction. Equation 2a is strictly valid for aqueous solutions of moderate viscosity⁷ but is assumed to be relevant also for the gelation process considered in this work. This will be discussed in more detail in subsequent sections.

If species other than paramagnetic ions are dissolved in water, the paramagnetic ions themselves might interact with these species to form chemical bonds (perhaps by complex formation) and thus modify the effective magnetic moment of the paramagnetic ion. If we assume the water molecules exchange fast, on an NMR time scale, between the different paramagnetic sites or environments, the overall relaxation rate of the water protons can be described by a generalized version of eq 2a:

$$1/\eta T_i = (K_i/kT) \sum_j \mu_{\text{eff},j}^2 C_j \quad i = 1, 2 \quad (2b)$$

where C_j defines the concentration of paramagnetic ions in site j (or environment j) with an effective magnetic moment $\mu_{\text{eff},j}$. The other symbols were already defined in eq 2a. Two independent NMR time signals (intensity vs time τ) denoted the transverse,

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$M_{xy}(\tau)$, and the longitudinal, $M_z(\tau)$, magnetizations are traditionally measured by the so-called spin echo and inversion recovery pulse sequences, respectively,¹¹ where the two magnetizations are written

$$M_{xy}(\tau) = M_0 \exp(-\tau/T_2) \quad (3a)$$

$$M_z(\tau) = M_0(1 - 2 \exp(-\tau/T_1)) \quad (3b)$$

M_0 is the equilibrium magnetization, τ is time, and $1/T_2$ and $1/T_1$ define the two relaxation rates. For paramagnetic solutions these NMR parameters are mainly controlled by the interaction between the electronic spin of the paramagnetic ion and the nuclear spin of the neighboring water protons.¹²⁻¹⁵ However, if the concentration of paramagnetic ions is relatively low, the interaction between the nuclear spins of the water protons (the diamagnetic contribution) must be considered as well, but this effect is of marginal importance in this work.

In the case of a so-called multiexponential behavior of the time-dependent magnetization, eq 3 must be modified:¹⁶

$$M_{xy}(\tau) = \sum_i M_{0i} \exp(-\tau/T_{2i}) \quad (4a)$$

$$M_z(\tau) = \sum_i M_{0i}(1 - 2 \exp(-\tau/T_{1i})) \quad (4b)$$

where M_{0i} is the longitudinal equilibrium magnetization of the water protons in phase i . The other symbols were previously defined in eq 3. Such a multiexponential behavior is characteristic of the existence of isolated "phases" or environments between which the water molecules are exchanging slowly.

Experimental Section

Preparation of Gel Solutions. The xanthan polymer used in this study was obtained as a 3% fermentation broth from Statoil-Biosentrum. The product quality and testing procedures are described in detail elsewhere.¹⁷ The intrinsic viscosity was measured to within 5000 cm³/g and filterability tests and the Huggins constant revealed a low tendency of the polymer to aggregate; thus it possesses a low initial entanglement. The viscosity corresponds to an average molecular mass of approximately 4×10^6 Da.¹⁸ A stock solution of 1 mass % of xanthan was prepared by direct dilution of a broth with artificial seawater. All solutions were stirred thoroughly for 15 min before use. The chromium ion was introduced as $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and dissolved in distilled water to give a stock solution of 0.1 M Cr^{3+} . Different gel solutions were prepared by mixing the two stock solutions thoroughly in well-defined volume ratios before loading them into the rheological measuring cell or the NMR magnet. A total reaction volume of 40 mL was used in the NMR experiments.

Instrumental Procedures. Determination of the storage modulus G' vs reaction time was performed on a Bohlin rheometer operating in an oscillating mode at a fixed frequency of 0.126 Hz and at a temperature of 25 °C. The instrument is remote-operated from an IBM PC. The NMR measurements were performed at 20 °C on a NMR Tomograph (Philips Gyroscan S15) operating at 1.5 T (corresponding to a proton resonance frequency of 60 MHz). The relaxation times were measured at discrete intervals during gelation. Each T_2 measurement lasted less than 1 s while a T_1 measurement required 10 s or more, depending on the actual

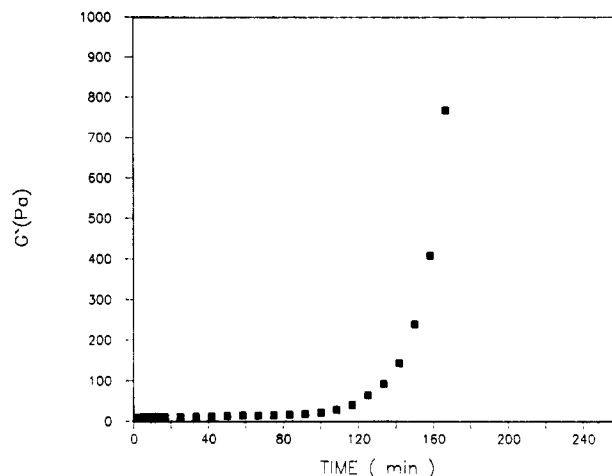


Figure 1. Storage modulus G' vs time during gel formation (8000 ppm of xanthan/2 mM Cr^{3+}).

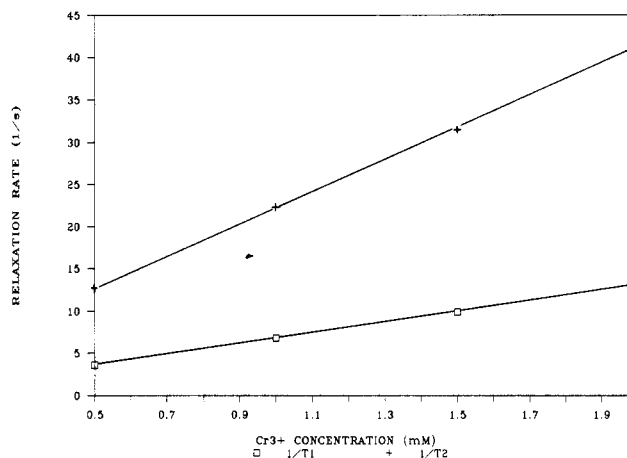


Figure 2. Spin-spin relaxation rate (+) and spin-lattice relaxation rate (□) of the solvent water protons vs Cr^{3+} concentration (mM).

spin-lattice relaxation time. Each series of experiments took about 4 h. The relaxation rates were determined by fitting eq 3 or 4 to the observed time-dependent magnetizations by a nonlinear least-squares technique.

Results and Discussion

Dynamical Storage Modulus. Figure 1 presents a typical plot of the storage modulus G' vs reaction time during the gel-forming process. The abrupt rise in G' after a certain time, denoted the "induction period" by Terry et al.,¹⁹ defines loosely the onset of cross-linking between polymers by formation of polymer-chromium-polymer links. During the induction period, where G' is nearly constant or slowly increasing with time, a low junction density or a small number of cross-links are being formed. This strong dependence of G' on number of cross-links makes this technique rather insensitive to other types of reaction mechanisms that might occur during the induction period. As seen in the next section, the ^1H NMR relaxation times are particularly affected during this time period, indicating that NMR spectroscopy is a convenient technique complementary to the oscillatory rheological analysis.

NMR Relaxation Rates. (a) Cr^{3+} Solution. Since the relaxation rates of the solvent water protons are known to be rather sensitive both to the external magnetic field strength and to the type of paramagnetic ion,^{12,15} the validity of eq 2 was explored in more detail. In particular, the need to estimate the sensitivity and the inherent uncertainty in the relaxation rates made such an analysis essential. The results are summarized in Figure 2 and reveal a relative uncertainty of less than 1% in these parameters.

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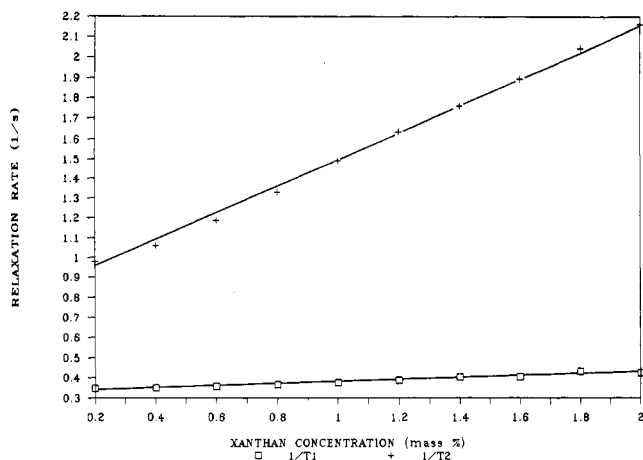


Figure 3. Spin-spin relaxation rate (+) and spin-lattice relaxation rate (□) of the solvent water protons vs xanthan concentration (mass %).

The reproducibility was found to be better than 5%. The sensitivity, expressed by the slopes of the lines in Figure 2, was determined to be 19.0 ± 0.1 and $6.3 \pm 0.1 \text{ s}^{-1} \text{ mM}^{-1}$ for the spin-spin and spin-lattice relaxation rates, respectively. Noting these results, we found it appropriate and advantageous to consider only the spin-spin relaxation rate in the subsequent discussion (due to its better sensitivity).

(b) *Xanthan Solution.* A corresponding analysis was also performed on water-xanthan solutions. The results are displayed in Figure 3 and are in agreement with what is expected from NMR theory. However, the two extrapolated straight lines predict significantly different relaxation rates at zero xanthan concentration. We believe this discrepancy to be caused by dissolved oxygen introduced into the solution during stirring. Since oxygen is paramagnetic, it will normally influence the spin-spin relaxation rate more rigorously than the corresponding spin-lattice relaxation rate. The difference will, however, also depend on the magnetic field strength.^{12,15} Both the transverse and the longitudinal magnetizations were described by single-exponential behavior (eq 3), confirming the assumption of a rapid exchange of water molecules, on an NMR time scale, between the polymer molecules and the "bulk" water phase. Hence, the results presented in Figures 2 and 3 can be summarized by the following expression:

$$(1/T_2)_{\text{obs}} = k'C_{\text{xanthan}} + k''C_{\text{chromium}} \quad (5)$$

where $(1/T_2)_{\text{obs}}$ is measured relative to the spin-spin relaxation rate of pure water and k' and k'' are empirical constants estimated from the observed data presented in Figures 3 and 2, respectively. C represents concentration. Thus, the observed relaxation rate is given by the sum of two contributing terms originating from the polymer and the paramagnetic species in the solution. Equation 5 is strictly correct if the xanthan molecules do not interact with the Cr^{3+} ions. As will be seen in the next section, this is indeed not the case. However, eq 5 is used to calculate the relaxation rate of the water protons at $t = 0$, i.e. the time at which the xanthan solution and the Cr^{3+} solution are mixed together. Note, in passing, that water protons confined in a solution of 0.8 mass % xanthan reveal a spin-spin relaxation rate which is less than 4% of that of water protons in a 2 mM Cr^{3+} solution.

(c) *Gelation.* The spin-spin relaxation rates vs gelation time of three chromium(III)-xanthan solutions, differing in their initial concentrations of xanthan and Cr^{3+} , are depicted in Figure 4. These NMR results appear somewhat unexpected when we consider rheological measurements that normally reveal a dramatic increase in both viscosity²⁰ and storage modulus G' (Figure 1) after the induction period. If the effective magnetic moment (μ_{eff}) remained constant during the gelation process, eq 2a would predict a corresponding increase in the spin-spin relaxation rate with time, which is in dramatic contrast to the observed decay of the re-

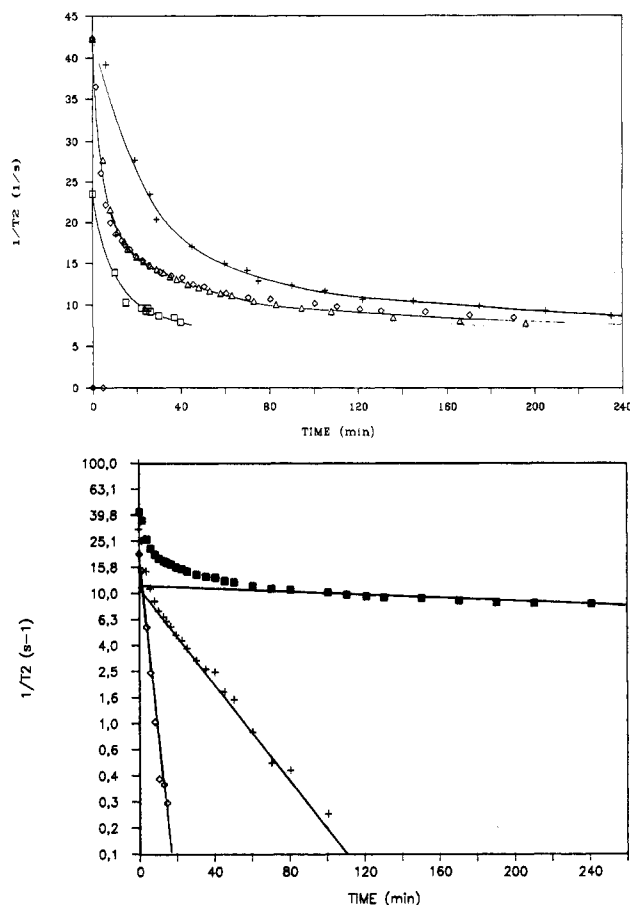


Figure 4. (a) Top: Spin-spin relaxation rate vs time during gel formation. Conditions: (Δ) 2 mM Cr^{3+} /8000 ppm of xanthan (1); (◇) 2 mM Cr^{3+} /8000 ppm of xanthan (2); (+) 2 mM Cr^{3+} /6000 ppm of xanthan; (□) 1 mM Cr^{3+} /6000 ppm of xanthan. (b) Bottom: Spin-spin relaxation rate vs time during gel formation. The solid lines illustrate the three different rates determined by fitting eq 10 to the observed data points (●); 2 mM Cr^{3+} /8000 ppm of xanthan. See text for further details.

laxation rate (Figure 4a). The only plausible explanation is therefore that μ_{eff} must decrease with time. Unfortunately, it is impossible from these NMR measurements alone to separate the two likely effects controlling the relaxation rate, namely changes in viscosity and changes in μ_{eff} for the paramagnetic species (eq 2a).

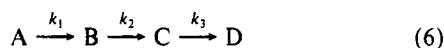
(d) *Viscosity.* Since the viscosity measured by rheological techniques reflects the macroscopic viscosity of the polymer network, it does not necessarily give any relevant information concerning the viscosity parameter (η) in eq 2. This viscosity factor is connected to the molecular freedom (translational and rotational movement) of the water molecules in the solution and is strongly related to the diffusion coefficient of the water molecules. Work published by Astarita²¹ showed that the diffusivities of small molecules in polymers were of the same order of magnitude as they were in pure water. This result leads naturally to the intuitive assumptions that the water molecules within the "cells" of the polymer network are tumbling freely, much as in bulk water, and that the viscosity term in eq 2 is constant in time and space (and approximately equal to the viscosity of bulk water). Hence, the results given in Figure 4 indicate that paramagnetism is the dominating relaxation mechanism due to the very small variations in relaxation rate at times when the viscosity and G' increase significantly, e.g. after about 100 min when substantial cross-linking is initiated (Figure 1). Note, however, that the relaxation rate is dependent on both the polymer concentration (comparing the results for 0.6% and 0.8% xanthan in a 2 mM Cr^{3+} solution) and the chromium concentration (comparing the results for 0.6% xanthan added to 1 and 2 mM Cr^{3+} solutions).

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Reaction Model

From the above discussion, the explanation for the observed time behavior of the spin-spin relaxation rate must be related solely to the effects of cross-linking on the effective magnetic moment of Cr^{3+} (eq 2b). As discussed by Bailey et al.,²² one mechanism for the gelation process involves the initial production of a chromic ion complex followed possibly by a cross-linking step occurring by olation. Further reaction steps might be possible, for instance oxalation.²² We will not go into any discussion concerning the details of the mechanism, which will be a major subject in our future NMR experiments, but simply assume that the different configurations of the xanthan-chromium(III) species are formed successively and irreversibly and that the process is characterized by a set of pseudo-first-order reaction steps, illustrated schematically as follows:



where A, B, C, and D represent different xanthan-chromium configurations with corresponding effective magnetic moments μ_A , μ_B , μ_C , and μ_D . The rate equations are easily derived (eq 8) and solved explicitly (eq 9) by taking into account the material balance with respect to the chromium "species" in eq 7, where C_0 is the initial chromium ion concentration. By inserting these

$$C_0 = [A] + [B] + [C] + [D] \quad (7)$$

$$d[A]/dt = -k_1[A] \quad (8a)$$

$$d[B]/dt = k_1[A] - k_2[B] \quad (8b)$$

$$d[C]/dt = k_2[B] - k_3[C] \quad (8c)$$

$$d[D]/dt = k_3[C] \quad (8d)$$

$$[A] = C_0 \exp(-k_1 t) \quad (9a)$$

$$[B] = C_0/(k_1 - k_2)[\exp(-k_2 t) - \exp(-k_1 t)] \quad (9b)$$

$$[C] = C_0/(k_2 - k_3)[\exp(-k_3 t) - \exp(-k_2 t)] \quad (9c)$$

$$[D] = C_0 - [A] - [B] - [C] \quad (9d)$$

concentrations into eq 2b, we obtain eq 10, where the k_i 's are the $1/T_2 = \alpha + \beta \exp(-k_1 t) + \gamma \exp(-k_2 t) + \delta \exp(-k_3 t)$ (10)

previously defined rate constants (eq 8). The coefficients α , β , γ , and δ are related to the parameters defined in eq 2b. Equation 10 was fitted to the experimental data by a nonlinear curve-fitting procedure. The relaxation rate at $t = 0$ was determined from eq 5 and used as a constraint or fixed point in the curve-fitting procedure. The results are shown by the solid curves in Figure 4a. The separation of the three different rate processes is illustrated in Figure 4b, where the observed spin-spin relaxation rates are subtracted successively from the calculated relaxation rates for each value of k_i . By comparing the data given in Figures 1 and 4, we note that the two initial processes $A \rightarrow B$ and $B \rightarrow C$ are more or less completed at the onset of the cross-linking step. One of these processes (probably $A \rightarrow B$) is most likely related to the initial reaction between a chromium ion and an active site on the xanthan molecule. The active site is probably the acid group on the glucose unit, which is located on the side chain of the repeating unit on the xanthan molecule. We have not been able to determine the structure of species C.

The observed decay of the spin-spin relaxation rate with time might equally well be explained by an alternative reaction scheme²³



where the reaction sequence for the net transformation of A to D proceeds via a reversible formation of intermediate C. The mathematical form of the relaxation rate equation can be shown to be analogous to eq 10. Most likely, the reaction step described by $C \rightarrow D$ in eq 6 or 11 is related to the cross-linking process. Note in particular that the NMR data seem to be rather sensitive to what is occurring in the induction period, in contrast to the rheological results (Figure 1), which give a significant response mainly after this time period. The two techniques are therefore complementary.

By varying the initial concentrations of reactants, we change the observed relaxation rate correspondingly. This is illustrated in Figure 4a but will not be discussed any further in this work. These results are included simply to demonstrate the significantly different progression of relaxation rate vs reaction time with varying initial conditions and indicate, accordingly, the potential advantage of the NMR relaxation technique.

The decay of the spin-spin relaxation rate with time is exclusively dependent on the effective magnetic moment of the individual xanthan-chromium configurations, as denoted by μ_A , μ_B , μ_C , and μ_D . If these magnetic moments were identical, no change in the spin-spin relaxation rate would be observable. It is worth noting that magnetic moments can be estimated from the curve-fitting procedure just outlined. The reaction models used in this analysis assume the Cr^{3+} ions to be completely transferred to one single environment, defined by species D. This presumption will certainly depend on the initial concentration ratio between xanthan and Cr^{3+} . Moreover, the reaction models seem to predict a relaxation rate that is independent of both the xanthan and the chromium ion concentrations. However, this concentration dependence is implicitly contained in the rate constants k_i , so the observed difference between the relaxation rates for different initial reactant concentrations is certainly not inconsistent with either of the two proposed models (eq 6 and 11). More thorough and comprehensive experimental work is needed in order to clarify the details of the kinetic model and to establish a more explicit reaction scheme.

Conclusion

This preliminary work has shown how ^1H NMR relaxation time measurements can be used to study the kinetics of so-called gelation processes. The method relies completely on the use of paramagnetic metal ions, but this is certainly not a crucial limitation since many similar types of processes involve such metal ions. However, not all paramagnetic metal ions are suitable because some of them, e.g. the metal ions Ce^{3+} and Ce^{4+} , possess too small an effective magnetic moment and therefore do not affect the relaxation rate of the water protons significantly. More systematic and comprehensive experimental work is needed in order to fully realize the potential and advantage of this technique in the field of gel formation processes. The convenience of combining rheology and NMR experiments is, however, clearly recognized in this work.

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