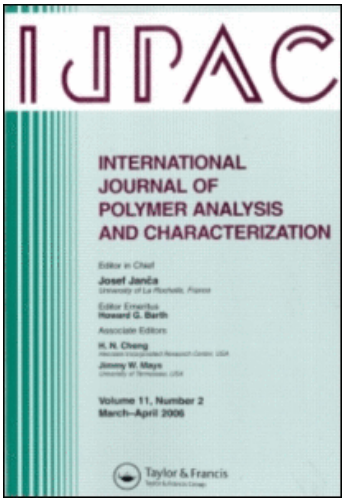

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Effect of Cr(III) Acetate Concentration on the ^{1}H NMR Behavior of HPAm/Cr(III) Acetate Gels

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Abstract: Partly hydrolyzed polyacrylamide-Cr(III) acetate (HPAm/Cr(III) acetate) aqueous gel systems formulated with HPAm to Cr(III) acetate weight ratios ranging from 5/1 to 60/1 and 5000 mg/L of HPAm were monitored using ^{1}H nuclear magnetic resonance (^{1}H NMR), bottle testing, and oscillatory rheology. The chemistry of the Cr(III) acetate complex dominated the ^{1}H NMR response of the formulations that did not form a continuous network structure. ^{1}H NMR detected gelation time and syneresis evolution in the formulations that rendered a continuous gel network structure.

Keywords: ^{1}H nuclear magnetic resonance; Hydrolyzed polyacrylamide-Cr(III) acetate gel; Oscillatory rheology

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INTRODUCTION

Nuclear magnetic resonance (NMR) methodologies have emerged as important techniques for polymer characterization. Although there is limited information about NMR characterization of aqueous partly hydrolyzed polyacrylamide-Cr(III) acetate (HPAm/Cr(III) acetate) gels, earlier studies indicate that NMR-based methodologies can be used to monitor changes in these gel systems.[1,2] HPAm/Cr(III) acetate gels are commonly applied in oil fields. These gels are viscoelastic, as their properties are intermediate to those of viscous liquids and elastic solids.[3] As the cross-linking reaction between HPAm and Cr(III) acetate proceeds, the viscous and elastic properties change,[2] which in turn causes a change in their molecular motions. NMR techniques are useful for investigating molecular motion. The time scale of molecular motions depends on the nature of the nuclei and the physical parameters such as mobility, viscosity, and temperature.[4,5] Previous work demonstrated that changes in the ^{1}H NMR transverse relaxation time (T_2) can be used to determine the gelation time (cross-linking time) of HPAm/Cr(III) acetate gels formulated with polymer concentration above the critical polymer concentration.[2] Experimental evidence that allows for correlating T_2 changes with gel syneresis for HPAm/Cr(III) acetate gels formulated with low polymer-to-cross-linker weight ratio (relatively high cross-linker loading) is presented. The objective of this work is to evaluate the effect of cross-linker (Cr(III) acetate) concentration on the ^{1}H NMR performance of gels formulated at 40°C with 5000 mg/L of HPAm and polymer-to-cross-linker weight ratios ranging from 5/1 to 60/1. The hypothesis is that changes in the behavior of T_2 can be used to determine gelation time and gel syneresis. The results presented coupled with previous findings[1,2,6] set a preliminary basis to develop an NMR method to monitor the gelation of bulk samples of HPAm/Cr(III) acetate gels in a noninvasive, nondestructive, and accurate manner.

LITERATURE REVIEW

Although the properties of HPAm/Cr(III) acetate gels mainly depend on the concentration and molecular weight of HPAm, they are also affected by the concentration of Cr(III) acetate.[7–10] An HPAm concentration higher than 2700 mg/L (critical polymer concentration for the HPAm used in this work) is needed to form a classical gel with a continuous cross-linked polymer network.[6] At constant temperature and HPAm concentration, increasing the Cr(III) acetate concentration increases the gel strength and rate of gelation where the optimum gel strength depends on the Cr(III) acetate concentration. Gels formulated with Cr(III) acetate

50% active concentrations higher than the optimum concentration (e.g., 2000 mg/L for the systems reported here) are prone to syneresis (expulsion of solvent from the gel), which negatively affects the gel performance in oil field applications. Generally, syneresis can be avoided by formulating the gel so as not to exceed the optimum cross-linker concentration. Formulations with relatively low Cr(III) acetate concentrations (e.g., 83 mg/L for the systems reported here) have an under-optimum gel strength. The optimum concentration of Cr(III) acetate increases with increasing temperature. It also decreases as HPAm molecular weight and HPAm concentration increase.[10]

^{1}H NMR characterization of HPAm/Cr(III) acetate gel components (in bulk) demonstrated that changes in T_2 strongly depend on the concentration and chemistry of Cr(III) acetate. Furthermore, the paramagnetic properties of Cr(III) acetate restrict the use of T_2 measurements to characterize gel formation of bulk samples (liquid-like) when the concentration of Cr(III) acetate 50% active is greater than 3000 mg/L. At higher Cr(III) acetate 50% active concentrations, the paramagnetism dominates, causing T_2 values to be short, and significant changes arising from other gel property phenomena are not observed.[1] At concentrations equal to or lower than 3000 mg/L of Cr(III) acetate 50% active, there are two contributions to T_2 when monitoring the gelation of one-phase bulk samples of HPAm/Cr(III) acetate: a contribution from the Cr(III) acetate chemistry and a contribution from changes in complex viscosity (η^*) during the gelation. For a system with two contributions to T_2, the relaxation is described by $T_{2\ observed}$ (or a single relaxation time), whose reciprocal is a weighted average of the reciprocals of the relaxation time contributions.[11] Thus, the two contributions are additive in rates, and in the case of the HPAm/Cr(III) acetate gels can be expressed as the normalized equation below where a is the weighting of the contribution from Cr(III) acetate chemistry:

$$1/T_{2\ observed} = a/T_{2\ Cr(III)\ acetate\ chemistry} + (1-a)/T_{2\ \eta^*changes} \qquad (1)$$

HPAm/Cr(III) acetate solutions formulated with polymer concentrations lower than the critical polymer concentration (2700 mg/L for the HPAm used) do not form a continuous gel network and η^* does not change significantly. As a result, the chemistry of Cr(III) acetate (molecular changes experienced by the Cr(III) acetate complex ion) dominates and becomes the main contribution to T_2.[6] Polymer solutions formulated with 7500 mg/L of HPAm and 3000 mg/L of Cr(III) acetate 50% active form a continuous gel network, and η^* increases as the gelation proceeds. Changes in η^* might have an effect on T_2 prior to cross-linking time.[2]

When HPAm/Cr(III) acetate gels undergo syneresis, the gel system consists of two phases: the gel and the solvent expelled from the gel.[12]

Preceding ^{1}H NMR studies have shown that the paramagnetism of Cr(III) strongly affects the T_2 relaxation of systems consisting of liquid and solid phases and containing concentrations of Cr(III) acetate 50% active greater than 2000 mg/L.[1] For two-phase systems (e.g., gel and syneresis phases in this study), $T_{2\ observed}$ is the weighted average of effects taking place separately in each phase.[11,13] For HPAm/Cr(III) acetate systems, $T_{2\ observed}$ can be expressed as Equation (2) where $H_{protons\ in\ the\ gel} + H_{protons\ in\ the\ solvent} = 1$, and solvent refers to the liquid syneresis phase:

$$1/T_{2\,observed} = H_{protons\,in\,the\,gel}/T_{2\,gel} + H_{protons\,in\,the\,expelled\,solvent}/T_{2\,expelled\,solvent} \tag{2}$$

At the experimental conditions used, the observed T_2 decay is given by an apparent mono-exponential function although there are two phases with different T_2 constants (which can be observed when phases are separated). Other ^{1}H NMR techniques can detect different relaxation times for each phase and a distribution of T_2 can be observed (details below). Polymer-free cross-linker solutions at 40°C with Cr(III) acetate 50% active concentrations lower than 100 mg/L are characterized by T_2 values greater than 2000 ms.[1] After gelation time, samples of gels formulated with Cr(III) acetate 50% active concentrations greater than 2000 mg/L have T_2 values lower than 300 ms.[2] The gels studied here are prone to syneresis when formulated with polymer-to-cross-linker weight ratios equal to or lower than 5/1, which is equivalent to concentrations of Cr(III) acetate 50% active equal to or greater than 2000 mg/L. As syneresis proceeds, the gel retains most of the cross-linker, therefore the concentration of Cr(III) acetate is greater in the gel phase than in the expelled solvent (syneresis phase). At the experimental conditions and parameters used, T_2 of the expelled solvent is greater than T_2 of the gel and Equation (2) can reduced to

$$1/T_{2\ observed} \approx 1/T_{2\ gel} \tag{3}$$

This work provides evidence that allows for considering T_2 measurements as a method to identify gelation time and to monitor gel syneresis of HPAm/Cr(III) acetate gels as they exist in bulk (e.g., glassware). Although gel syneresis can be prevented by formulating the gel without exceeding the optimum cross-linker concentration, a gel system prone to syneresis is studied here to evaluate the capability of ^{1}H NMR to detect changes in T_2 as the solvent (syneresis phase) separates from the gel. Since ^{1}H NMR T_2 detects syneresis solvent evolution, it could also detect other forms of separation of solvent from the gel, when placed in oil reservoirs, due to phenomena such as gel dehydration. ^{1}H NMR techniques can be applied in porous media.[14] Thus, these ^{1}H NMR functionalities can, in principle, be applied to monitor the

separation of solvent from the gel under conditions that represent oil reservoirs.

EXPERIMENTAL SECTION

Materials

The cross-linker used was commercial Cr(III) acetate ($Cr(OOCCH_3)_3$) solution 50% active in water (pH = 2.6) supplied by McGean-Rohco, Inc. The certificate of analysis (provided by McGean-Rohco) reports that there is less than 0.0001% of Cr(VI) in the Cr(III) acetate solution 50% active. Commercial HPAm (Alcoflood 935™, Ciba), distilled water, and Na_2SO_3 (oxygen scavenger) were used to prepare the polymer solutions. Alcoflood 935 has a manufacturer-reported degree of hydrolysis of about 10% and molecular mass of 8×10^6–10×10^6 g/mol. The concentrations of HPAm (as supplied) and Na_2SO_3 were 5000 mg/L and 100 mg/L respectively. Samples of 5000 mg/L HPAm solution were mixed with Cr(III) acetate 50% active at concentrations (in the final gelant solution) ranging from 166 to 2000 mg/L. In these samples the concentration of Cr(III) acetate ranged from 83 to 1000 mg/L. Table I lists the concentrations of Cr(III) acetate 50% active, the corresponding polymer-to-cross-linker weight ratios, and pH of the solutions used. A Corning pH meter 220 was used to measure the pH.

Experimental Procedures

Bottle Testing

Characterization of the gel samples, using Sydansk's gel strength code,[10] was conducted at 40°C. Three sister samples of each formulation were

Table I. HPAm to Cr(III) acetate weight ratios and pH of gelant solutions formulated with 5000 mg/L of HPAm

Cross-linker concentration, mg/L		Polymer-to-cross-linker weight ratio HPAm/Cr(III) acetate	pH 25°C
Cr(III) acetate 50% active	Cr(III) acetate		
166	83	60/1	6.03
250	125	40/1	5.81
500	250	20/1	5.46
1000	500	10/1	5.09
2000	1000	5/1	4.71

tested. The solutions formulated with polymer-to-cross-linker weight ratios ranging from 60/1 to 10/1 were tested for 10 days. The solution formulated with a weight ratio of 5/1 was tested for 60 days.

Monitoring Gel Syneresis

Seven sister samples, 55 mL each, of the HPAm/Cr(III) acetate (5/1) gelant solution were placed in 60 mL flint glass widemouthed bottles with polyvinyl-liner cap seals. The samples were kept in a water bath at 40°C and were monitored every 48 h during the first 10 days and every 240 h thereafter. The water expelled from the gel was withdrawn and its volume was measured using a 10 mL graduated cylinder following the procedure presented in the work of Bryant et al.[12] The ratio of volume of expelled water to volume of the original bulk gel sample (55 mL) was calculated. Gel syneresis was expressed as volume percentage of syneresis (% *syneresis in bulk* = (*expelled water volume* (*mL*)/*55 mL*) ∗ *100*). The expelled water removed from the gel sample was not replaced back into the original gel sample. It was kept in bottles at 40°C during the 60 days of testing. A logistic equation (sigmoid function) describes the rate at which syneresis progresses. Hence, the equation used to model the gel syneresis of the HPAm/Cr(III) acetate (5/1) is $\%\ gel\ syneresis = a/(1 + (t/x_o))^b$.

The solvent expelled from the gel samples was tested for Cr(VI) using a diphenyl carbazide colorimetric procedure, which is a standard method from the U.S. Environmental Protection Agency (EPA) designated as EPA 7196a. The samples were also tested for total chromium content using inductively coupled plasma emission spectrometry (ICP-ES) in conjunction with EPA Method 200.7. The chromium speciation tests were performed by the Research and Productivity Council (RPC), Fredericton, N.B., Canada.

Rheology

An Anton Paar Physica MCR 301 rheometer with concentric cylinder geometry (CC27) was used. A sweep time of 9 h was conducted on the gel formulated with a polymer-to-cross-linker weight ratio of 5/1, at 40°C, with frequency of 1 Hz and amplitude of 5%. This test was performed by Anton Paar USA. Details about the rheometer used and the viscoelastic properties of HPAm/Cr(III) acetate gels are presented elsewhere.[1,2,6] In this work, gelation time (or cross-linking time) is defined as the time at which the storage modulus (G') and loss modulus (G'') curves intersect.[15,16]

^{1}H NMR T_2 Measurements

The transverse relaxation times (T_2) of the gels were measured using a Bruker Minispec model mq10 NMR Analyzer. Three sister samples of each formulation were tested using a Carr-Purcell-Meiboom-Gill (CPMG)[15] pulse sequence with echo time = 0.25 ms, recycle delay = 15 s, gain = 80 dB, and number of scans = 64. The number of echoes ranged from 10000 (solution with a polymer-to-cross-linker weight ratio of 5/1) to 54000 (solution with a weight ratio of 60/1). The measuring time ranged from 21 to 31 min. The temperature of the NMR probe was kept constant at 40°C. The solutions formulated with polymer-to-cross-linker weight ratios of 10/1, 20/1, 40/1, and 60/1 were tested for 10 days. The solutions formulated with a weight ratio of 5/1 were tested for 60 days to monitor gel syneresis. More details about T_2 measurements are presented elsewhere.[1,2,6]

T_2 measurements conducted on the HPAm/Cr(III) acetate (5/1) gel samples during the first 9 h were compared to η^* changes (from rheological measurements). This gel experienced syneresis, and after syneresis occurred, the expelled solvent was kept in the NMR sample vials. Thus, subsequent NMR measurements were conducted on the sample consisting of both separate gel and expelled solvent phases. The HPAm/Cr(III) acetate (5/1) gel contains 2000 mg/L of Cr(III) acetate. At this concentration, the paramagnetism of Cr(III) strongly affects T_2 relaxation,[1,2] and if the fractional size of one phase is less than approximately 10%, this phase will not be resolved with the Minispec and CPMG sequence used. Thus, a distribution of T_2 is not observed. Rather, T_2 decayed following a mono-exponential function. With the progression of syneresis, the gel becomes more rigid (most of the cross-linker remains in the gel), and the solvent separates from the gel, carrying a small concentration of cross-linker (see below). Compared with the separated solvent (which has a T_2 above 2000 ms), the T_2 of the gel is short (300 ms or less), due to its high cross-linker concentration and solid-like state. Short T_2 values are best detected with small echo time, such as the 0.25 ms used, and long T_2 values are best detected with long echo time (e.g., 1.1 ms). T_2 is sensitive to echo time,[17] and to avoid the effect of echo time on T_2, the CPMG parameters were kept constant in this study.

Although a well-defined bi-exponential decay of T_2 might be expected, the T_2 obtained with the CPMG parameters employed was best fitted with mono-exponential decay (R^2 was greater than 0.99 in all cases). T_2 measurements conducted on the HPAm/Cr(III) acetate (5/1) gel (which undergoes syneresis) after 720 h tend to have a bi-exponential decay. Yet, to allow for comparison of the T_2 behavior throughout syneresis, a mono-exponential model was used to determine the

$T_{2\ observed}$. T_2 measurements from 192 to 1440 h were correlated to gel syneresis. To determine the T_2 constants of each phase, the gel and the expelled solvent (syneresis phase) were separated at the end of testing (at 1441 h). T_2 of the gel was measured with an echo time of 0.25 ms and 10000 echoes, and T_2 of the expelled solvent was acquired with an echo time of 1.1 ms and 16000 echoes. ^{1}H NMR measurements using different CPMG parameters or techniques can be used to further investigate syneresis using a bi-exponential model. Allen et al.[18] reported the use of a modified CPMG sequence (referred to as a new multi-wait CPMG) to improve T_2 measurement in multiphase systems.

RESULTS AND DISCUSSION

Bottle Testing

The effect of polymer-to-cross-linker weight ratio on 5000 mg/L HPAm solution was monitored based on the differences in gel strength codes.

Table II. Gel strength codes from bottle testing[10] for HPAm/Cr(III) acetate 50% active formulated at 40°C with 5000 mg/L of HPAm

	HPAm to Cr(III) acetate 50% active weight ratio				
Time hours	60/1	40/1	20/1	10/1	5/1
0.0	A	A	A	A	A
3.5	A	A	A	A	B
13	A	A	A	A	B
18	A	A	A	B	C
24	A	A	B	B	C
30	A	A	B	B	C
48	A	A	B	B	D
72	A	A	B	C	D
96	A	A	B	C	E
144	A	A	B	C	E
168	A	A	B	C	F
192	A	A	B	C	*
240	A	A	B	C	*
1440	—	—	—	—	*

A: no detectable gel formed; B: highly flowing gel; C: flowing gel; D: moderately flowing gel; E: barely flowing gel; F: highly deformable nonflowing gel; *: gel exhibits syneresis, —: bottle testing was not conducted.

Table II lists the results obtained from bottle testing. The gel strength code of A was assigned to the HPAm/Cr(III) acetate (40/1) and (60/1) solutions during 240 h of bottle testing at 40°C. A gel strength code of A is assigned when there is no visually detectable gel formed, which means that the HPAm/Cr(III) acetate solution appeared to have the same viscosity (fluidity) as the original polymer solution and no gel is visually detectable.[10]

Changes in the sample color were not observed in the 40/1 and 60/1 formulations because the concentration of Cr(III) acetate is not high enough to color the polymer solution. Fresh HPAm/Cr(III) acetate (20/1) solution had a green color, which is characteristic of chromium acetate cyclic structure and oxalate groups.[19] This solution turned blue after 10 h, and a gel strength code of A was assigned for the first 18 h of formulation aging. At 24 h and over a period of 240 succeeding hours, the solution was categorized as highly flowing gel and the gel strength code of B was assigned.

Cao Xu-long et al.[20] found that for polyacrylamide-based systems there is a critical cross-linker concentration below which these systems do not form a continuous 3-D gel network. Based on the bottle testing findings at 40°C, formulations with 5000 mg/L of the HPAm (Ciba's Alcoflood 935™) and the solvent used (solution of 100 mg/L Na_2SO_3 in distilled water) have a critical cross-linker concentration greater than 500 mg/L of Cr(III) acetate 50% active. This corresponds to a polymer-to-cross-linker weight ratio greater than 20/1.

Increasing the concentration of cross-linker increases the gel strength and the rate of gelation.[10] Thus, as the concentration of Cr(III) acetate increased (the polymer-to-cross-linker ratio decreased), the changes in the gel strength code occurred faster (Table II) as a result of the formation of continuous gel network structures. Fresh HPAm/Cr(III) acetate 50% active (10/1) gelant solutions were green, then progressively changed to green-blue, and after 18 h they turned blue and remained blue until the end of testing (240 h).

According to Tackett,[19,21] Cr(III) acetate (chromic triacetate) in solution experiences hydrolysis when aged or heated and the cyclic structure becomes a blue linear structure. Tackett[21] reports that HPAm with a degree of hydrolysis greater than 5% prevents Cr(III) acetate hydrolysis. Nonetheless, the results of this work show that the HPAm used, which has a degree of hydrolysis (as reported by manufacturer) of 10%, does not prevent the color change (from green to blue) that is typical in Cr(III) hydrolysis. The HPAm/Cr(III) acetate 50% active (5/1) turned blue after 24 h. The subsequent tests focused on this last gel formulation because it experienced more changes in its physical properties (e.g., syneresis) than the other gel systems.

Syneresis of HPAm/Cr(III) Acetate 50% Active (5/1) Gel

The beginning of gel syneresis for this gel system was evident after 192 h when a volume of 2.2 mL solvent was expelled from the gel (4% of the gel initial volume, referred to as percent of gel syneresis). At the end of the testing (1440 h), 38.8 mL of gel solvent (72% of the gel's initial volume) was expelled from the gel due to syneresis. Figure 1 depicts the progression of syneresis as percent of syneresis (which is equivalent to the percentage of solvent expelled from the gel due to syneresis) as a function of time.

Cr(VI) speciation tests conducted on 60-day-old samples of solvent expelled (pH = 4.6) from the gel indicated that there is a Cr(VI) concentration lower than 0.05 mg/L (STDV = 0). These results are in agreement with the certificate of analysis provided by McGean-Rohco, which reports less than 0.0001% of Cr(VI) in the Cr(III) acetate 50% active, and also confirm that during the gelation of the system evaluated at 40°C oxidation of Cr(III) to Cr(VI) does not occur. A speciation test for total Cr content yielded a concentration of 58.6 mg/L (STDV = 6.2). 6.2). Compared to the fresh gel, the chromium concentration of the solvent expelled from the gel is lower by a factor of 17. In 60 days, the gel lost 5.9% of the original chromium concentration during syneresis.

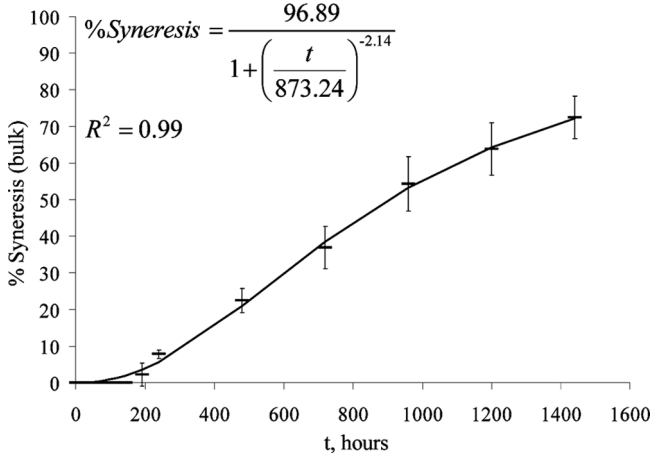

Figure 1. Cumulative percentage of gel syneresis as a function of time for HPAm/Cr(III) acetate 50% active (5/1) gels at 40°C.

Rheology

Figure 2 depicts the changes in loss modulus (G''), storage modules (G'), complex viscosity (η^*), and damping factor ($\tan\delta = G''/G'$) experienced

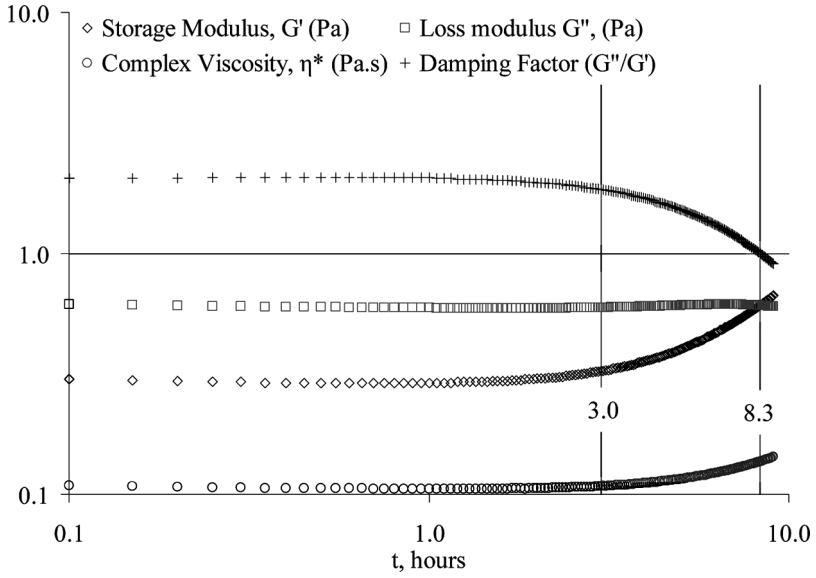

Figure 2. Rheology of a HPAm/Cr(III) acetate 50% active (5/1) gel at 40°C.

by the HPAm/Cr(III) acetate 50% (5/1) gel during the 9 h of testing. G'' decreased slightly from 0.61 to 0.59 Pa, G' increased from 0.30 to 0.67 Pa, and η^* increased from 0.10 to 0.14 Pa · s. At 8.3 h, G' and G'' are equal to 0.608 Pa and G''/G' is equal to 1 ($\tan\delta = 1$), which gives a measure of the gelation time. Below 8.3 h, G'' is greater than G' and the HPAm/Cr(III) acetate 50% active (5/1) gel behaved more like a viscous liquid. After the gelation time, the elastic component dominated and the gel behaved more like an elastic solid. The rheology monitoring was conducted only for 9 h since during this time T_2 changes the most, and the goal of this work is to compare T_2 changes to rheological changes. More rheological research is planned to characterize HPAm/Cr(III) acetate gels over longer periods.

^{1}H NMR Measurements

The T_2 of polymer-free Cr(III) acetate 50% active solutions formulated with concentrations lower than 2000 mg/L at 40°C decreased within the first 24 h, after which T_2 gradually increased.[2] Hydrolysis and molecular changes of the Cr(III) acetate complex ion in solution[19, 21] might be related to changes in the $T_{2\ observed}$ in the cross-linker solutions. HPAm/Cr(III) acetate 50% active systems formulated with 5000 mg/L of HPAm and polymer-to-cross-linker weight ratios of 20/1, 40/1, and 60/1

exhibited the same general T_2 behavior as the polymer-free Cr(III) acetate 50% active solutions. T_2 decreased during the first 24 h and progressively increased thereafter during the 240 h of the testing (Figure 3). T_2 increased at a rate of 0.69 ms/h for the 40/1 and 60/1 systems and 0.60 ms/h for the 20/1 system. The 40/1 and 60/1 gels appeared to have the same fluidity as the 5000 mg/L HPAm solution (Table II) and did not form a continuous gel network. Although the 20/1 gel was slightly more viscous than the 5000 mg/L HPAm solution, it did not appear to form a continuous gel network either.

The ^{1}H NMR relaxation behavior of HPAm/Cr(III) acetate systems that do not form continuous gel network structures is dominated by the chemistry of Cr(III) acetate.[6] The rate at which T_2 increases with time is lower for higher concentrations of cross-linker, as the paramagnetism of Cr(III) reduces the relaxation times. T_2 is also inversely proportional to viscosity.[4,5] When the complex viscosity (η^*) of HPAm/Cr(III) acetate gels increases, T_2 will be reduced, but the magnitude of the effect is lower than that from the Cr(III) chemistry.[2] Fluidity of the 10/1 system changed (based on bottle testing results) with η^*. Compared to the 20/1, 40/1, and 60/1 systems, the T_2 of the 10/1 system increased at a slower rate (0.21 ms/h), due to the higher Cr(III) concentration and increased viscosity.

Figure 4 shows the T_2 behavior of the HPAm/Cr(III) acetate 50% active (5/1) gel system as a function of time and a cross-linker solution

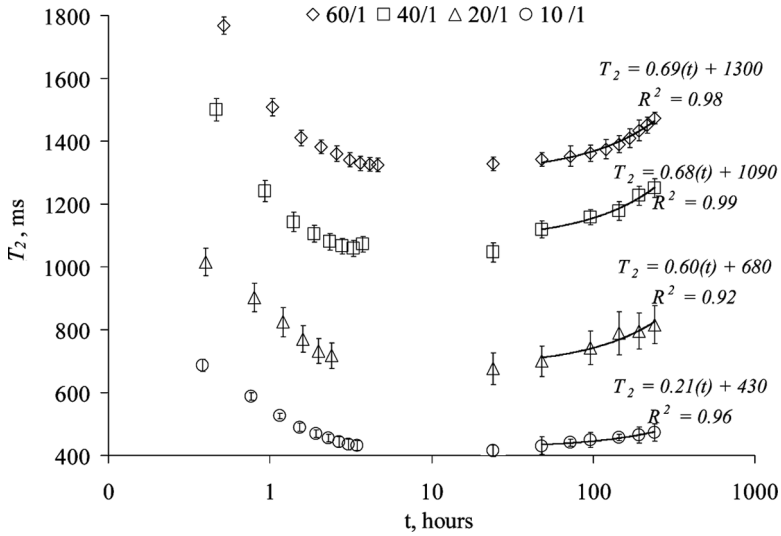

Figure 3. T_2 of gels formulated at 40°C with 5000 mg/L of HPAm and HPAm to Cr(III) acetate 50% active weight ratios ranging from 60/1 to 10/1.

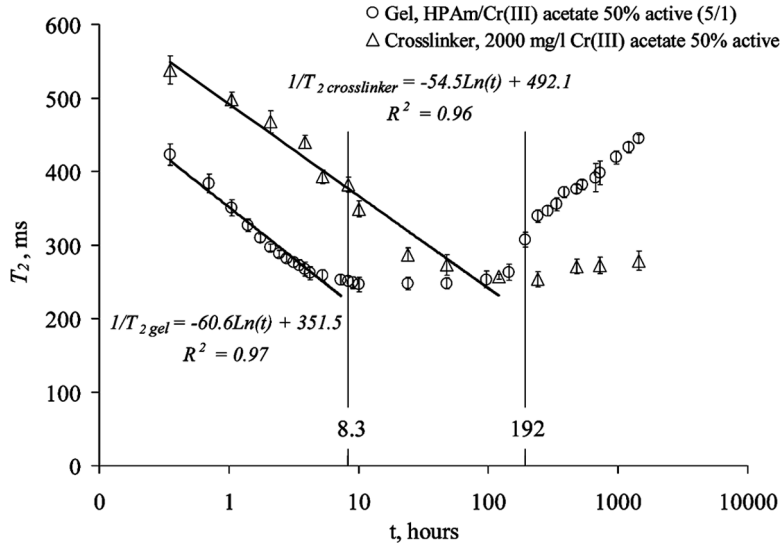

Figure 4. T_2 of HPAm/Cr(III) acetate 50% active (5/1) gel at 40°C.

formulated with 2000 mg/L of Cr(III) acetate 50% active (the same concentration used for the gel). The shapes of the gel formulation and the cross-linker solution curves are similar from 0 to 192 h, which suggests that the relaxation mechanism at work is the same but in different time scales. Figure 4 shows that the T_2 of the gel and the cross-linker decreases in similar fashions and reaches a minimum value around 250 ms. For both systems, the curves of T_2 as a function of time exhibit steady periods after 250 ms. These results imply that the chemistry of the Cr(III) acetate complex might be the main contribution to the changes in T_2.

The gel-forming solution did not experience significant rheological changes during the first 3 h (Figure 2), yet T_2 decreased by a factor of 1.5, following the same trend as the cross-linker solution. After 3 h, η^* of the gel solution began to increase (Figure 2) as T_2 reduction continued. T_2 became stable at 8.3 h, when the rheological gelation time was observed. HPAm/Cr(III) acetate 50% active systems that form a continuous gel network exhibit a stable T_2 after cross-linking time.[2] This is true for the HPAm/Cr(III) acetate (5/1) gel studied here. Figure 4 shows that at 8.3 h T_2 is equal to 249 ms and remains almost constant for 168 h, when it is equal to 254 ms (a difference of 5 ms is not considered experimentally significant).

Although the T_2 behavior of the cross-linker solution is similar to that of the gel (from 0 to 192 h), T_2 changes are observed at different time scales. This difference might be due to the presence of the polymer (in the

gel) and possibly the effect of the complex viscosity on T_2. Figure 5 shows the rate at which $1/T_2$ changes as η^* changes from 0 to 8.3 h. Even though η^* is not the main contribution to T_2 changes throughout the cross-linking reaction, it might accelerate the rate at which T_2 of the gel reaches the minimum value (compared to the 2000 mg/L Cr(III) acetate 50% active solution).

Syneresis was observed at 192 h when $T_{2\ observed}$ was equal to 307 ms. Up to 240 h, the fractional size of the solvent expelled from the gel was less than 10%, and therefore the $T_{2\ observed}$ decayed following a mono-exponential function (see above). As syneresis proceeded, $T_{2\ observed}$ increased with time and reached 445 ms, or $1/T_{2\ observed}$ decreased with time and reached $2.25 \times 10^{-3}\,\mathrm{ms}^{-1}$, at 1440 h (Figure 5). The total chromium concentration in the solvent expelled from the gel (58.6 mg/L) is 17 times lower than the original concentration in the gel (see above).

At 40°C and 1441 h (60 days), T_2 from the expelled solvent (without the gel phase) is 2369 ms and T_2 of the gel (without the syneresis phase) is 134 ms. Based on these results, Equation (3) can be applied (as the T_2 of the solvent is much greater than T_2 of the gel) to correlate the rate at which $1/T_2$ changes ($1/T_{2\ observed}$) with the rate at which gel syneresis proceeds. According to the results from chromium speciation, is reasonable to assume that the expelled solvent collected from gels in the bottles has

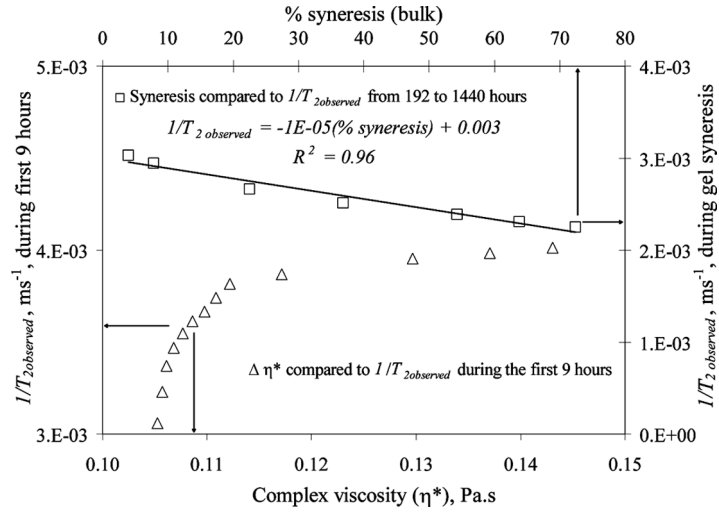

Figure 5. Complex viscosity (η^*) and syneresis of the HPAm/Cr(III) acetate 50% active (5/1) gel compared to $1/T_{2\ observed}$ at 40°C. (Δ) shows η^* compared to $1/T_{2\ observed}$ evolution during the first 9 h after gel formulation. (□) represents the correlation between the rate of gel syneresis and $1/T_{2\ observed}$ from 192 to 1440 h.

the same ^{1}H NMR properties as the expelled solvent in the NMR vials. Thus the changes in $1/T_{2\ observed}$ can be compared to the percent of syneresis, as presented in Figure 5. An empirical correlation between $1/T_{2\ observed}$ and percentage of syneresis can be modeled by a straight line equation ($R^2 = 0.96$) with a slope equal to –1E-5 (% syneresis $\cdot$ ms^{-1}) and a y-intercept equal to 0.003 ms^{-1} ($1/T_{2\ observed}$ at 0% syneresis). This correlation is the evidence that ^{1}H NMR can be used to monitor syneresis of HPAm/Cr(III) acetate gel.

CONCLUSIONS

T_2 measurements can be used to monitor changes as HPAm/Cr(III) acetate 50% active gels age. However, more research is required to accurately determine the effect of complex viscosity changes on T_2 behavior of HPAm/Cr(III) acetate gels. Bottle testing indicated that a continuous network gel was formed when the polymer-to-cross-linker weight ratio is less than 20/1 for gels formulated with 5000 mg/L of HPAm and under the experimental conditions of this study. ^{1}H NMR detected changes in T_2 caused by the combined effect of Cr(III) acetate chemistry and complex viscosity in HPAm/Cr(III) acetate gel systems that form a continuous network. The complex chemistry of the Cr(III) acetate dominated the T_2 behavior of the HPAm/Cr(III) acetate 50% active aqueous solutions that did not form a continuous gel network structure.

The gelation time of the HPAm/Cr(III) acetate 50% active (5/1) gel was determined as the time at which T_2 becomes stable, at 8.3 h. This time was in agreement with the rheological gelation time. Direct observations of HPAm/Cr(III) acetate 50% active (5/1) gel changes through bottle testing indicated that this gel underwent syneresis after 192 h at 40°C. Syneresis was also detected by ^{1}H NMR when T_2 started to increase after 192 h. This T_2 behavior allowed for correlation of the rate of syneresis with the rate at which T_2 increased. Therefore, the proposed hypothesis is supported as changes in T_2 performance can be used to determine gelation time and the onset of gel syneresis.

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