Delayed HPAM Gelation via Transient Sequestration of Chromium in Polyelectrolyte Complex Nanoparticles

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Received January 29, 2008; Revised Manuscript Received March 24, 2008

ABSTRACT: Heterogeneity of oil reservoirs often leads to unproductive cycling of injected oil recovery chemicals, resulting in the loss of significant quantities of reserves. To maximize recovery efficiency, a blocking agent may be placed deep into high-permeability channels so that the subsequently injected chemicals can be redirected into previously unswept regions. Cr(III)−polyacrylamide gels have been used extensively in field applications as blocking agents for sweep improvement; however, the gelation time of the current state-of-the-art is too short to achieve in-depth placement. This paper describes a novel approach of using polyelectrolyte complex nanoparticles to entrap and control the release Cr(III) to effectively extend gelation time. Self-assembly of polyethylenimine (PEI) and dextran sulfate (DS) resulted in the formation of ∼100−200 nm particles that efficiently entrapped chromium while maintaining colloidal stability in water or gelant. Although the addition of chromium chloride to HPAM typically produced gels in minutes, chromium was efficiently sequestered in nanosuspensions of polyelectrolyte complexes, resulting in a significant delay in gel formation that was dependent on pH, ionic strength, and temperature. The gel formation kinetics of PEI, polyelectrolyte complexes (PECs) of PEI and DS, and PECs loaded with chromium were compared. PEI, a known cross-linker of HPAM, produced a steady increase in gelant viscosity over time. PECs without chromium demonstrated a delayed gel formation compared to PEI but possessed a similar creeping increase in viscosity. In contrast, PECs loaded with chromium typically showed minimal viscosity increase over time followed by an abrupt viscosity increase, resulting in gel formation. This study suggests that PECs offer a flexible nanotechnology platform that may enable novel chemical delivery schemes in the oil and gas industry.

Introduction

In improved oil recovery (IOR) operations, reservoir heterogeneity often results in unproductive cycling of injected IOR chemicals, leaving significant otherwise recoverable reserves behind. To successfully improve sweep efficiency, a blocking agent must be placed deep into the reservoir to effectively plug the high-permeability channels so that the subsequently injected chemicals may be diverted into the previously unswept hydrocarbon-rich zones.[1,2] Cr(III)−polyacrylamide gels have been used extensively in field applications for water shutoff and sweep improvement.[3–10] During placement, the polymer solution is injected with the cross-linking agent into the formation to allow gelation to occur in situ.[8–11] Once the gel is set, it can no longer propagate through formation rock since injection rate is limited by the hydraulic conductivity of the formation, rock strength, logistics, and pump power.[12] Therefore, long gelation time (in days, weeks, or even months) is required to achieve in-depth placement. The current state-of-the-art relies mostly on ligands such as acetate and propionate to form complexes with Cr(III) ions to delay gelation.[13–16] However, the gelation time of the current state-of-the-art is too short (hours) for in-depth placement.[10,17] This may limit applications to near wellbore regions or fractured wells.[9,10,18]

Competing problems exist when designing a controlled release delivery system for delaying gelation. Larger particles such as microspheres may be desired for delaying release due to the increased diffusional path length in comparison to nanoparticles; however, microspheres may settle out of solution or impede penetration into reservoir rocks due to size-exclusion effects.[12,19] On the other hand, nanoparticles less than a few hundred nanometers in diameter generally demonstrate colloidal stability as a result of convective motion in the carrier fluid and/or by engineering the nanoparticle surface to impede agglomeration (e.g., via steric hindrance or electrostatic repulsion). Unfortunately, the short diffusive path lengths for entrapped cross-linkers may result in rapid release and minimal delay in gelation kinetics. Since colloidal stability and size are key requisites for propagating controlled release agents suspended in gelling solution deep into the formation rock, it becomes important to address the problem of rapid cross-linker release from nanoparticles. One possible mechanism to delay release from nanoparticles is to generate a binding event that selectively retains the cross-linking agent within the nanoparticle matrix so that diffusion is encumbered by electrostatic binding events.

Nanoparticle polyelectrolyte complexes (PECs) may be formed by self-assembly of highly charged polycations and polyanions through electrostatic intermolecular interactions. PECs have proven effective for entrapping and delivering small molecules, peptides, large proteins, and even DNA and typically maintain colloidal stability via electrostatic repulsion.[20,21] A variety of PECs may be fabricated by changing the chemical composition of polymers, including molecular weight, flexibility, functional group structure, charge density, hydrophilicity, etc.[22] Self-assembly also depends on the concentration of each polyelectrolyte in the mixture, the ionic strength of media, and the solution pH.[23] PECs formed via the self-assembly of polyethylenimine (PEI) and dextran sulfate (DS) in solution were selected to encapsulate the cross-linker Cr(III) due to their high charge density and potential for transiently sequestering charged agents (Figure 1). Middaugh et al. previously reported methods using these polyelectrolytes where the PECs were cross-linked by adding zinc sulfate.[24–26] This effort, designed to improve

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10.1021/ma800211d CCC: $40.75

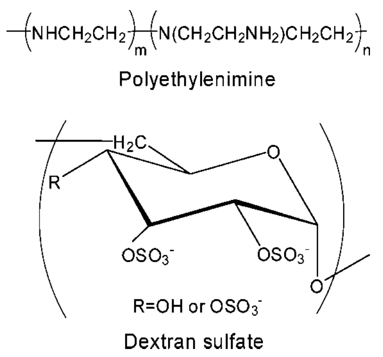

Figure 1. Chemical structures of polyelectrolytes employed.

nanoparticle stability when delivering therapeutics, led to the hypothesis that an ionic cross-linker for HPAM such as Cr(III) may be transiently sequestered in PECs through binding events within the nanoparticles.

This paper describes a novel approach of using PECs to entrap and control the release of Cr(III) in an effort to extend gelation time. PECs were formed by adjusting the total concentration of PEI and DS as well as the ratio of these polyelectrolytes. The resulting nanoparticles were $<$200 nm in diameter and could be endowed with a positive or negative zeta potential (i.e., surface charge), resulting in colloidal stability. Cr(III) ions were entrapped into PECs by simply adding chromium chloride salt to the PEC suspension. Cr(III) ions were entrapped with high efficiency ($>$90%), and excess chromium was removed by dialysis. The time to HPAM gelation was varied from hours to days by controlling the relative concentration of PEC nanoparticles and the vessel temperature. Robust and persistent gels were formed and a potential mechanism was deduced. A wave of research continues to endow PECs with properties for improving performance; however, this work represents the first example of PEC use for oil and gas field applications to our knowledge.

Materials and Methods

Materials. Dextran sulfate (M_w = 500 kDa, Fisher Scientific) and polyethylenimine (M_w = 25 kDa, Aldrich) were used as obtained without further purification. Partially hydrolyzed polyacrylamide (HPAM; M_w = 6000 kDa), AlcoFlood 935, Lot A2247BOV, was purchased from Ciba Specialty Chemicals. Chromium chloride ($CrCl_3 \cdot 6H_2O$, M_w = 266.45, Fisher Scientific) was used as a gelation cross-linker. Calcium chloride, sodium hydroxide, and hydrochloric acid were obtained from Fisher Scientific and used as received.

Preparation of Polyelectrolyte Complex Nanoparticles. A typical method to prepare chromium (Cr)-loaded polyelectrolyte complex (PEC) nanoparticles was as follows. A 10 000 mg/kg aqueous solution of DS (15.32 g) was added dropwise to 34.26 g of a 10 000 mg/kg aqueous solution of PEI and stirred for 15 min at 600 rpm. Then, 1.0 mL of a Cr stock solution was injected and stirred for another 30 min. The Cr stock solution (~100 000 mg/kg in $CrCl_3 \cdot 6H_2O$, which is ~19 500 mg/kg in Cr(III)) was fresh made by dissolving $CrCl_3 \cdot 6H_2O$ in deionized water. The prepared particles were dialyzed against deionized water for 48 h using Spectra/Por CE dialysis membrane with a MWCO of 100 kDa.

Characterization of Polyelectrolyte Complex Nanoparticles. The mean PEC particle size was determined by dynamic light scattering experiments employing a ZetaPALS zeta potential analyzer (Brookhaven Instruments Corp.). An aliquot of nanoparticles was diluted with deionized water, and three consecutive 1 min measurements were obtained by detecting light scattering at a 90° angle. The mean effective diameter and polydispersity were determined by the method of cumulants.[27] The zeta potential of the particles was investigated by phase analysis light scattering using the same instrument. The samples were measured using 1−1.5 mL of 1 mM KCl solution. The zeta potential was calculated from the electrophoretic mobility using the Smoluchowski approximation. Three measurements were taken for each sample.

Determination of Cr Concentration. Cr concentrations were determined by oxidizing Cr(III) to Cr(VI) and measuring the UV−vis absorbance at a wavelength of 373 nm following reported procedures.[16] Oxidation of the Cr was accomplished by mixing 0.5−1.0 mL of Cr(III) samples with 1.0 mL of 3% H_2O_2 and 1.0 mL of 1 N KOH and heating the mixture for 1 h at 87 °C. The oxidized samples were then diluted to Cr(VI) concentration between 1 and 10 mg/kg by adding deionized water. A Perkin-Elmer Lambda-20 UV−vis spectrometer was used to measure UV absorbance of Cr(VI) at ambient temperature. The Cr(III) concentration in the sample was determined using a Cr(VI) concentration vs UV absorbance standard curve at 373 nm. Relative standard deviations of less than 0.1% were typical for 11 absorbance measurements on a given sample. Concentration in the original solution was calculated by multiplying by the appropriate dilution factor.

Cr Entrapment Efficiency. The entrapment efficiency of Cr into polyelectrolyte nanoparticles was calculated by an indirect method where Cr concentration was determined in supernatant following centrifugation of a sample and subtracted from the initial amount added to the nanoparticle suspension. Freshly made nanoparticles were centrifuged at 13 000 rpm for at least 20 min. The supernatant was collected for the Cr concentration measurement. The entrapment of Cr was calculated as follows.

$$\text{entrapment efficiency} = \frac{[Cr^{3+}]_0 - [Cr^{3+}]_s}{[Cr^{3+}]_0} \times 100\%$$

where $[Cr^{3+}]_0$ and $[Cr^{3+}]_s$ are the Cr(III) concentrations entered into the experiment and measured in the supernatant after mixing with particles, respectively.

Preparation of Gelants. First, a 20 000 ppm HPAM stock solution was prepared by dissolving solid HPAM in a 4% (w/w) NaCl, 400 ppm NaN_3 solution. A container with a known amount of brine was vigorously stirred to create a deep vortex. Polymer was slowly added to the shoulder of the vortex to effectively wet the polymer beads. The container was sealed to minimize evaporation and was stirred continuously for 48 h to ensure complete dissolution of polymer. The stock solution was optionally filtered through a 0.3 μm cellulose filter under a driving pressure of 15 psi. The HPAM stock solution was mixed with deionized water and then the dialyzed particles. The amounts of the three components were carefully tuned so that the final gelant contained 5000 ppm HPAM and 100 ppm Cr(III) in a 1% (w/w) NaCl, 100 ppm NaN_3 solution. The gelant was stirred for a few minutes until a visually homogeneous solution was obtained. Then the gelant was kept in an oven at constant temperature and allowed to gel.

Measurement of Gel Time under Various Conditions. A Brookfield digital viscometer (Model DE-I+) was used to monitor the viscosity to determine the gel time of the gelants. The gel time was defined as the time when the viscosity of the gelant increased abruptly to a value $>$1028 cP at a shear rate of 2.25 s^{-1}. The temperature of the viscometer was controlled at 25 °C. In some experiments, a calcium chloride solution (11 250 ppm) was added to produce various final calcium concentrations. Deionized water was added in each case to make up the remaining volume to produce the desired final concentration. In other experiments, 0.1 N hydrochloric acid (HCl) or 0.2 N sodium hydroxide (NaOH) was added to produce the desired gelant pH. The remaining volume was again made up by adding deionized water.

Results

Effect of Polyethylenimine on the Kinetic Viscosity of HPAM. Polyelectrolytes employed in this study may interact with HPAM and cause a change in viscosity. Polyethylenimine (PEI) has been shown to cross-link HPAM and lead to the formation of gels at high temperature;[28,29] therefore, it was

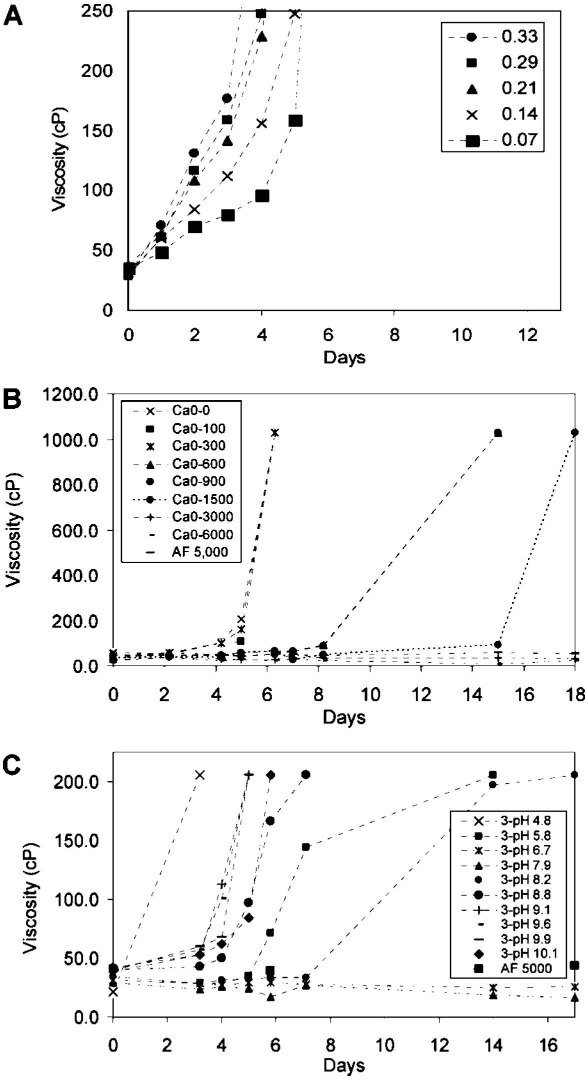

Figure 2. (A) Polyethylenimine mixed in different weight ratios to polyacrylamide resulted in a concentration-dependent, rapid increase in viscosity. (B) Increasing calcium delays gel formation in the PEI/polyacrylamide system. (C) The formation of gels was also impacted by gelant pH. Low pH values (6.8 or less) led to instantaneous gel formation while a pH value of 10.8 mitigated gel formation over the course of 6 days. Unless otherwise noted, experiments included 5000 ppm polyacrylamide at 40 °C using a shear rate of 11.25 s^{-1}.

important to determine the effect of polyelectrolytes on gel formation as a baseline for comparison. PEI was included with HPAM in different weight ratios to HPAM while holding the HPAM concentration constant at 5000 ppm. Increasing the concentration of PEI led to a corresponding increase in the rate that viscosity increased (Figure 2A). The results suggested that PEI immediately interacted with polyacrylamide to form aggregates and that the degree of interaction between PEI and HPAM chains steadily increased over time. The other polyelectrolyte used to form PECs, dextran sulfate, was also introduced to the HPAM polymer system; however, no significant kinetic viscosity change was observed.

The increase in viscosity in the PEI/HPAM gel system was also sensitive to the presence of divalent cations and pH. Calcium chloride was added in different concentrations to solutions of HPAM (final concentration, 5000 ppm), and then PEI was added to the system (final concentration, 500 ppm). The kinetics of viscosity enhancement remained consistent up to 600 ppm of calcium chloride, showing a steady increase in viscosity over time prior to a more rapid transition to a gel (Figure 2B). Increasing calcium concentration led to a corresponding decrease in the initial gelant viscosity and a delay in the onset of gel formation. A slight increase in viscosity over time was still somewhat evident. Modulating the pH of the PEI/HPAM gel system also resulted in perturbations in gel formation kinetics (Figure 2C). Gels did not form at 6.7−7.9 pH values during a 2 week study, but pH values above and below this range resulted in steady increase in viscosity over time to varying degrees. A more detailed discussion of mechanistic pH effects in this system and in the PEC system is offered in the Discussion section. Cumulatively, the performance of the PEI/HPAM gelant serves as a backdrop for understanding the mechanism of PEC gel formation with and without the inclusion of Cr.

Preparation of Polyelectrolyte Complexes. PECs were readily obtained by controlling the concentration of each polyelectrolyte stock solution and the mixing ratio as previously reported.[21,24–26,30] Generally, polyelectrolyte concentrations of 1% (w/v) or less and mixing ratios >1:1 wt PEI:wt DS (dextran sulfate) were required to form positively charged PECs. Decreasing the polyelectrolyte weight ratio allowed the production of negatively charged PECs, exhibiting a DS corona. Ratios were tuned to reproducibly create PECs less than 200 nm. An example of a commonly used procedure is reported in the Methods section. Systematic methods for controlling particle size and surface charge are available in previously published works referenced above, which offer more detailed information on PEC production and variables.

Performance of PECs in Delaying Gel Formation. In theory, PEI may cross-link HPAM and form robust gels in a delayed manner if PEI is temporarily bound with another polyanion that occupies PEI binding sites with HPAM. To this end, PECs were formed by simply mixing PEI and DS with the hypothesis that DS may transiently block PEI/HPAM interactions. PECs of PEI and DS were formed with a particle size of 117.9 nm and a zeta potential of 27.9 ± 5.7 mV. In repeated experiments, polydispersity values were <0.3, suggesting a moderately narrow particle size distribution. The pH of PEC suspensions was typically ~9 as a result of the strong buffering capacity of PEI.

The PEC nanoparticles were added in different weight ratios (weight nanoparticles to weight HPAM) while keeping the concentration of HPAM constant at 5000 ppm in the gelant. The pH of gelants including PECs was ~9. Increasing the concentration of PECs caused a faster increase in gelant viscosity as expected (Figure 3A). Interestingly, reducing the weight ratio of PECs led to a more defined transition point between steadily increasing viscosity and rapid viscosity enhancement leading to gel formation. The decreased time to gel formation for lower PEC concentrations was somewhat counterintuitive. Data from the HPAM gel formation when mixed with unloaded PECs (Figure 3) have led to several hypotheses of possible mechanisms driving gelation. It is possible that residual free PEI chains and/or the positively charged particles themselves may have induced the initial phase of steadily increasing viscosity (Figure 3A). Changes in the onset time of the second phase of more rapid viscosity enhancement may result from a concentration effect on the competition of HPAM for DS binding sites with PEI. For example, the increase in the weight ratio of PECs to HPAM would decrease the relative number of HPAM interactions with PECs and perhaps delay the disruption of PEI/DS bonds. In comparison to the PEI/HPAM system, increases in viscosity were not as rapid.

Temperature also showed an effect since a lower temperature (~23 °C) resulted in a decrease in the gelant viscosity enhancement rate (Figure 3B). This result may be expected given that the kinetic motion of molecules increases at higher temperatures, which is anticipated to increase the mobility of

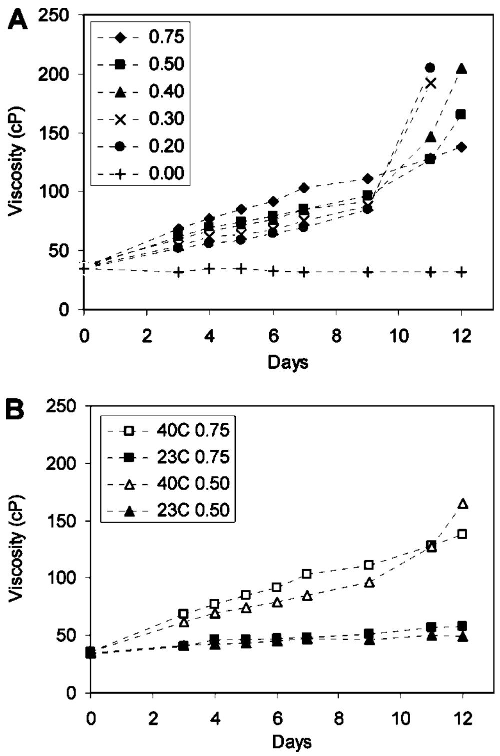

Figure 3. (A) Polyelectrolyte complexes included in different weight ratios showed steadily increasing viscosity followed by a more rapid viscosity enhancement that was dependent on concentration and on (B) temperature. Experiments included 5000 ppm polyacrylamide at 40 °C using a shear rate of 2.25 s^{-1}, except when another temperature is noted.

macromolecules and the probability of breaking PEI/DS bonds and forming PEI/HPAM cross-linking interactions. Studies of PECs entrapping Cr support this hypothesis since the gelation kinetics demonstrated Arrhenius behavior (see below).

PECs Efficiently Entrapped Cr. PECs were found to efficiently entrap Cr via a simple addition of a solution of chromium chloride to the PEC suspension. Several ratios of DS:PEI were studied to establish colloid formulations that efficiently entrapped Cr and that demonstrated colloidal stability (Table 1). The DS:PEI ratio of 0.45 was selected for the ability to delay the gelation of HPAM, and two batches of PEC nanoparticles (I, II) were prepared at this ratio (Table 2). All the stock solutions including the PEI, DS, and Cr stocks were freshly made for each batch. The data were reproducible for different batches. The particle size was less than 200 nm, and the polydispersity values were all <0.20, indicating reasonably narrow size distributions. PECs loaded with Cr fabricated with a DS:PEI ratio of 0.45 also possessed positive surface charges, similar in magnitude to unloaded PECs. Dialysis did not significantly change the size and the zeta potential of the nanoparticles studied. Again, the pH value of PEC suspensions remained relatively high level due to the buffering capacity of PEI. The Cr concentration in the nanoparticles decreased during dialysis due to the removal of the small amount of free Cr. The average entrapment efficiency typically ranged from 93−95% as shown in these exemplary experiments (Table 2).

PECs Entrapping Cr Delayed Viscosity Increases. Gelants with various concentrations of PEC nanoparticles and HPAM were investigated to determine the dynamic effect of Cr-loaded PECs on gelant viscosity. PECs containing Cr were added in different weight ratios (weight nanoparticles to weight HPAM) while keeping the concentration of HPAM constant at 5000 ppm (Figure 4A). For all concentrations studied, PECs containing Cr showed similar lag phases with minimal increase in viscosity over 4 days. The lag was followed by an abrupt increase in viscosity leading to relatively rapid gel formation. Adding a ratio of 0.30 of Cr-loaded PECs:HPAM (~100 ppm Cr) delayed gel formation and produce a robust gel at 2000 ppm HPAM (Figure 4B). A shorter lag phase was observed in the gelant containing 2000 ppm compared to the gelants containing 5000 ppm HPAM. In addition, PECs that did not contain Cr were not able to form gels in the 2000 ppm HPAM gelant even when higher weight ratios of PECs were added (0.45), at least during the time frame studied. Unloaded PECs did produce a steady increase in gelant viscosity (Figure 4B) as in the 5000 ppm HPAM studies (Figure 2).

A systematic study of the effects of ionic strength and pH was conducted to compare the performance of PECs entrapping Cr to the PEI/HPAM system. For these studies, gelants included 5000 ppm HPAM and 0.30 wt PECs/wt HPAM, which translated to ~100 ppm Cr in the gelant. Similar to the observations in the PEI/HPAM gelant, increasing the concentration of calcium chloride resulted in a corresponding decrease in the rate of viscosity increase after the lag phase (Figure 4C). In this figure, the lines serve as a guide to the eye and do not indicate that gelation started to occur on day three. Increasing the calcium concentration also led to a slight decrease in the initial gelant viscosity. High concentrations of calcium (>500 ppm) impeded the formation of gels over the time frame studied, which corroborated the data observed in the PEI/HPAM system.

Viscosity profiles for the same gelant system (0.30 PECs, 5000 ppm HPAM, ~100 ppm Cr) were also sensitive to pH (Figure 4D). The normal gelant pH was ~9. When gelant pH was lower than ~7, the solution gelled in less than 1 h. A pH of 8 led to a more steady increase in viscosity and mitigation of the typical viscosity transition observed in the Cr-loaded PEC system. A pH value of 10.8 caused no appreciable change in viscosity over the course of 6 days. For comparison, a pH value of 6.7 produced no viscosity change in 17 days in the PEI/HPAM gelant (Figure 2C); however, a similar pH of 6.8 in the Cr-loaded PECs/HPAM gelant produced robust gels in <1 h (Figure 4D). Both experiments were conducted at 40 °C. It should be noted that the gelant possessed a strong buffering capacity around pH 9−9.5 when PEI or PECs were used. Further discussion of these findings and mechanistic considerations are offered in the Discussion section.

Cr-loaded PECs reproducibly formed HPAM gels at the same time, and the viscosity profiles were dependent upon temperature (Figure 5). Gelants were prepared by splitting two separate preparations of Cr-loaded PECs that had been dialyzed against RO water through a 100 kDa MWCO cellulose membrane to remove free Cr (Table 2). The final gelants contained 5000 ppm HPAM and ~100 ppm Cr(III) as before, with a pH value of ~9.3. The gelation study was conducted at 40 °C. The four samples demonstrated similar viscosity profiles and gelled after 4.5 days, thus suggesting significant reproducibility in the Cr-loaded PEC delivery system (Figure 5A). In contrast, control gelants consisting of 5000 ppm HPAM and 100 ppm Cr (also from $CrCl_3 \cdot 6H_2O$) formed gels in less than 30 min.

The same gelants (0.30 PECs, 5000 ppm HPAM, ~100 ppm Cr) were subjected to different temperatures to determine the effect on viscosity profiles (Figure 5B). Increasing the temperature of gelants led to a significant reduction in the lag phase prior to gel formation. In addition, the application of higher temperatures (60 and 80 °C) produced some viscosity increase during the lag time before gel formation, although the gelant viscosity was held to <50 cP for more than 5 h even at these high temperatures. Gelants containing the Cr-loaded PEC delivery system demonstrated a strong dependence on temper-

Table 1. Properties of Representative PEC Formulations as a Function of DS/PEI Ratio

DS/PEI concn ratio (ppm/ppm)	DS (g)	PEI (g)	Cr^{3+} (ppm)	entrapment efficiency (%)	particle size	polydispersity	zeta potential
2.22[a]	17.15	7.66	377.50	81.3	133.7 ± 3.0	0.091 ± 0.025	−25.21 ± 0.97
0.92	11.91	12.9	377.01		the sample precipitated		
0.45[a]	7.66	17.15	377.76	91.6	146.0 ± 1.5	0.152 ± 0.036	15.15 ± 0.96
0.25	4.92	19.92	377.31	81.4	170.7 ± 1.2	0.171 ± 0.044	19.81 ± 3.45
0.12	2.66	22.2	377.01	82.4	160.3 ± 4.6	0.210 ± 0.034	21.68 ± 2.03

[a] Selected for gelant studies.

Table 2. Properties of Cr-Loaded PECs

sample		diameter (nm)	polydispersity	zeta potential (mV)	pH	entrap eff (%)
I	before dialysis	170	0.15 ± 0.04	22.9 ± 2.2	9.70	
	after dialysis	153	0.15 ± 0.03	17.8 ± 2.3	8.96	94.3
II	before dialysis	173	0.16 ± 0.01	20.2 ± 1.5	9.63	
	after dialysis	151	0.10 ± 0.02	16.4 ± 2.4	8.99	93.6

ature, which corroborated the temperature dependency noted in the unloaded PEC gelant (Figure 3B).

Discussion

The current state-of-the-art relies mostly on the greater kinetic stability of Cr(III)−ligand complexes to delay the cross-linking of Cr(III) ions with polymers such as HPAM.[13−16] Cr(III)−acetate−HPAM is the most widely used gel system for IOR applications where acetate is used as the ligand to form complexes with Cr(III) ions.[8,13,18] However, the gelation time of the most commonly used Cr(III)−acetate−HPAM gel system is only around 5 h at 40 °C,[10] which is too short for in-depth placement in matrix rock. In contrast, the gelation time for the comparable Cr(III)−PEC−HPAM system used in this study is 4.5 days at 40 °C. One possible way to increase the gelation time that has been reported is to use stronger ligands such as malonate and glycolate;[14] however, degelation could also occur when the binding with Cr(III) gets too strong.[31]

PECs' performance in delaying the cross-linking of HPAM may be due, at least in part, to the transient sequestration of Cr ions in PECs. PEI is known to be a potent chelator of many metal ions, including Cr,[32,33] and sulfated polymers such as the DS have also been reported to bind metals, including Cr.[34] Cr forms both amine and sulfate salts; therefore, solutions of chromium chloride were mixed with 1% solutions of each polyelectrolyte to gauge interactions by assessing the formation

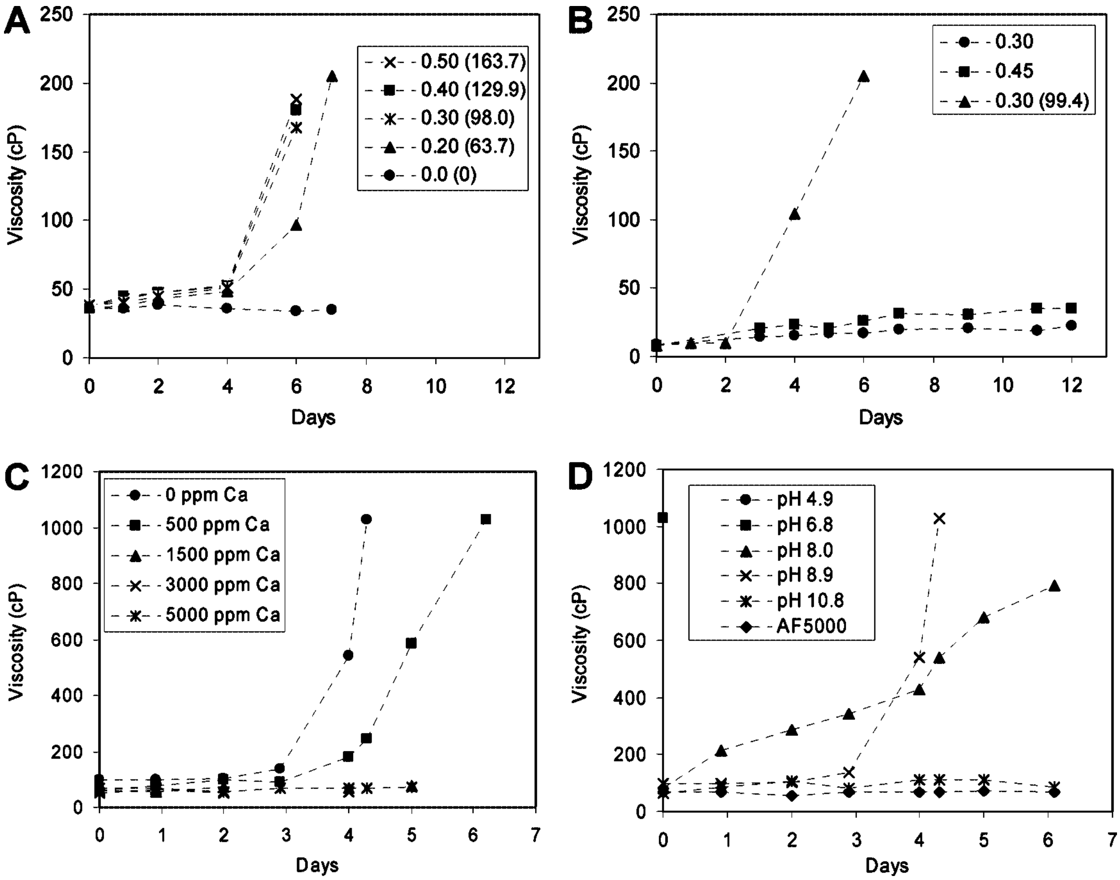

Figure 4. (A) Polyelectrolyte complexes entrapping chromium were mixed with 5000 ppm polyacrylamide. This formulation demonstrated delayed viscosity increase with rapid gelation that was dependent on concentration (chromium concentration denoted in parentheses). (B) Polyelectrolyte complexes including 99.4 ppm chromium were also able to maintain low solution viscosity followed by rapid gelation for 2000 ppm polyacrylamide in comparison to similar concentrations of polyelectrolyte complexes. (C) The gelation time for polyelectrolyte complexes (0.30 weight ratio PECs: HPAM) entrapping chromium (~100 ppm) was delayed as a result of increasing calcium concentration in solution. (D) For the same system, low pH values (6.8 or less) led to instantaneous gel formation while a pH value of 10.8 mitigated gel formation over the course of 6 days. Experiments were conducted at 40 °C using a shear rate of 2.25 s^{-1} for (A) and (B) and using a shear rate of 11.25 s^{-1} for (C) and (D).

Table 3. Aggregation in Chromium/Polyelectrolyte Mixtures[a]

	diameter (nm)	polydispersity	appearance
1.53 g 1% DS + 100 μL Cr stock	210	0.27 ± 0.03	green, clear solution, low particle count
3.43 g 1% PEI + 100 μL Cr stock	139	0.14 ± 0.05	grayish green, cloudy
PECs	170	0.15 ± 0.04	grayish green, cloudy

[a] Cr stock solution (∼100 000 mg/kg of $CrCl_3 \cdot 6H_2O$, which is ∼19 500 mg/kg of Cr(III)).

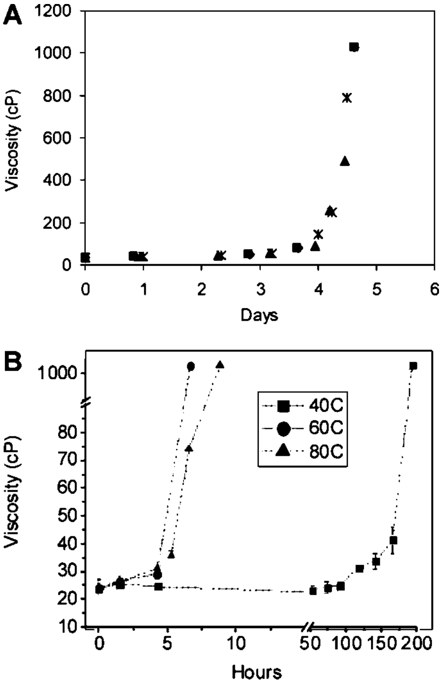

Figure 5. (A) Delay in HPAM gel formation at 40 °C was highly reproducible as shown in data overlaid from four experiments. (B) Viscosity profiles were dependent on temperature with higher temperatures leading to shorter gelation times ($n = 3$). Experiments were conducted using 5000 ppm HPAM and 0.30 wt Cr-loaded PECs/wt HPAM (∼100 ppm Cr) at a shear rate of 11.25 s^{-1}.

of aggregates. Concentrations were chosen to reflect the relative amounts of PEI or DS and Cr added into a typical experiment to form PECs (Table 3). Aggregates on the order of 150−200 nm were detected in each mixture of Cr with individual polyelectrolytes. The count rate, however, for DS mixture with Cr was very low and produced a green, transparent solution, which was similar in appearance to the solution of Cr alone. Previous reports also suggest that the interaction of Cr with DS may be weak and easily disrupted by sodium ions.[34] The count rate for the PEI mixture with Cr was significantly higher, exhibiting a count rate and grayish green appearance similar to the typical PEC formulation where Cr was added after PEI/DS PECs have formed. These results suggested that PEI was primarily responsible for binding Cr ions and entrapping them in the PECs.

To further probe this hypothesis, negatively charged PECs were fabricated by using the mass ratio of PEI/DS of 2.22 (Table 1). Nanoparticles were produced exhibiting a similar size to the positively charged PECs; however, negatively charged particles were produced as a result of the excess DS. In addition, the properties of negatively charged PECs significantly changed after dialysis, suggesting that this formulation was not as stable as the positively charged PECs (Table 4). The reduced concentration of PEI also reduced the buffering capacity of the PEC suspension, which led to a reduction in pH from ∼9.3 to ∼6.6 during dialysis. Gelants were formed containing either ∼100 or ∼50 ppm Cr entrapped in negatively charged PECs in 5000 HPAM, and the viscosity was tracked over time. Both gelants transitioned to rigid gels rapidly, overnight at 40 °C and in 2 h at 80 °C. Since gels formed much more quickly when the relative weight of PEI was reduced, it is probable that the presence of PEI in PECs played a significant role in temporarily binding and delaying the presentation of Cr ions. In addition, the excess sulfates in DS may have competed for Cr binding sites on PEI leading to more rapid Cr release. Finally, gels formed slowly (days) or not at all in the PEI/HPAM system at pH values between 6 and 8; therefore, it is unlikely that the rapid gel formation in negatively charged PECs could be attributable to PEI cross-linking HPAM.

Table 4. Properties of Negatively Charged, Cr-Loaded PECs

sample	diameter (nm)	polydispersity	zeta potential (mV)	pH	entrap eff (%)
before dialysis	180	0.26 ± 0.03	−29.4 ± 2.2	9.27	
after dialysis	113	0.18 ± 0.03	−25.9 ± 1.2	6.62	86.0

The effect of calcium concentration and pH may also provide an effective tool for modifying the delay in gel formation. Calcium concentration has previously been shown to effect the nature of HPAM cross-links.[35] For example, low concentrations of calcium (serving as the cross-linker) or low concentrations of carboxyl groups (low hydrolysis percentage) were reported to produce intrachain cross-links. Increasing either calcium or carboxyl groups produced an increased probability of forming interchain cross-links leading to gel formation. Calcium delayed viscosity increases in the Cr-loaded PEC/HPAM gelants, suggesting that calcium may be occupying Cr binding sites on HPAM. Alternatively, one may suspect that calcium may displace Cr ions within the PECs; however, this would likely lead to faster gelation as calcium concentration increased, which was not observed.

The pH of gelants provides an additional means to control the viscosity profile in PEC/HPAM gelants. PEI/HPAM viscosity profiles were significantly affected by pH (Figure 2). At pH values <5, PEI has an extremely high charge density ($>48\%$ of nitrogens protonated) so PEI may be rapidly pairing with carboxyl groups in the HPAM structure. At pH >8 essentially all the carboxyl groups should be negatively charged, and ∼7% of the amine groups should be protonated; therefore, the carboxyl groups in the long HPAM chains may drive gel formation by hosting PEI guest cations. Gel formation may be somewhat mitigated at intermediate pH values in the PEI/HPAM system since there would be minimal charge on the carboxylic acid around pH 5.5 or 6. The rapid transition to a robust gel in gelants containing Cr-loaded PECs (Figure 4) indicated that a substantial number of cross-links were formed by Cr since the viscosity increase as a result of PEI forming cross-links was generally slower (Figures 2 and 3). Usually, the use of inorganic salts of Cr constrains the preparation of gelants to values below pH 5.8 due to chromium precipitation as chromium hydroxide.[36] Robust gels reproducibly formed at significantly higher pH values in the Cr-loaded PEC/HPAM gelant that strongly buffered the pH around 9. Presumably, Cr interactions with hydroxide ions were hindered by PEI, and Cr exchange with free carboxyl groups was favored over precipitation. This observation may facilitate applications for inorganic salts of Cr in oil fields. PECs themselves were observed to be stable at all pH values ≤ 10.

Finally, a release study was conducted to provide further insight into the mechanism of delayed gel formation. For this study, suspensions of positively or negatively charged PECs were prepared, and Cr release was detected by using a dialysis membrane or centrifugation to separate the Cr associated with PECs. In each study, less than a few percent of the Cr was ever released, which strongly suggested that the Cr will interact with PECs as long as they are present in suspension. This observation indicated that the presentation of Cr to HPAM must occur as a result of interactions between PECs and HPAM. Taking this into consideration and comparing data in Figure 3, one may speculate that HPAM interactions with PECs may displace Cr ions, leading to the formation of gels. This hypothesis, however, does not seem to adequately address the reason for the very rapid kinetics of gelation observed for the Cr-loaded PECs.

Conclusions

A flexible nanoparticle system based on charged polymers has been demonstrated to delay the formation of HPAM gels. In this scalable process, oppositely charged polymers are self-assembled in solution by simply mixing low concentration stock solutions of each polyelectrolyte. The resulting PECs possessed small size (<200 nm), colloidal stability, and efficiency in entrapping chromium ions. When included with HPAM, a stable and homogeneous nanoparticle suspension was observed, and gel formation was effectively delayed for several days. The same gelant composition without PEC nanoparticles gelled in 30 min. Future work will aim to systematically investigate other polyelectrolytes and cross-linkers as a method to effectively modulate the onset time of gel formation for a variety of pH and temperature values. As an extension of this nanotechnology, active ingredients such as scale inhibitors, corrosion inhibitors, surfactants, cross-linkers, etc., have also been encapsulated in our laboratories. In addition, this methodology allows one to control the size and surface charge of the colloids, which may offer flexibility in modulating the passage or retention of nanoparticles as an approach to localize molecules of interest.

Acknowledgment. The authors thank the various organizations that have provided laboratory support including the state of Kansas through the Tertiary Oil Recovery Project, the American Heart Association, the Cystic Fibrosis Foundation, the DOD (W81XWH-07-1-0021), and the NIH (1R03 AR054035-01A1, P20 RR016443 and P20 RR015563). Special thanks to Russ Middaugh for the use of laboratory equipment.

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MA800211D