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Coordination Chemical Concepts Applied to the Design of Metal Ion Crosslinked Polymer Gels

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Eight novel acrylamide co-polymers containing from 0.7–4.5 mol % metal ion-chelating co-monomers have been prepared. The gelation chemistry of aqueous solutions of these co-polymers has been examined in the presence of Cr^{+3} and B^{+3} ions. Chemical and rheological evidence is presented which shows that the chelating functional groups modify both the thermodynamic and kinetic stabilities of the crosslinking complexes formed with these ions relative to those formed with hydrolyzed polyacrylamide.

KEY WORDS Chromium-polymer gels, boron-polymer gels, metal ion crosslinks, chelating polymers, water-soluble polymers

INTRODUCTION

Metal ion crosslinked polymer gels find a number of important uses in the field of petroleum production.¹ These include well-established applications such as the hydraulic fracturing of reservoir rock, carried out in order to increase well productivity,² and experimental applications in enhanced oil recovery (EOR).³ In the EOR applications a fluid solution of the polymer and metal ion crosslinker is pumped into the porous reservoir rock in order that, after gelation takes place, the flow of injected or reservoir fluids within the reservoir will be advantageously modified. The current or potential importance of these gel-based technologies has stimulated considerable research activity aimed at identifying polymer gel compositions possessing the necessary crosslinking rate, physical properties, and stability to reservoir conditions.^{3,4}

Crosslinking in metal ion/polymer gels comes about through the formation of chemical bonds between the metal ions and polymer-bound functional groups. Because gelation generally occurs only under conditions in which the metal ion-polymer complexation (crosslinking) reaction is favored thermodynamically, it fol-

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lows that a given metal ion will only crosslink polymers bearing specific functional groups and only under certain conditions of pH, ionic strength, concentration of the reagents, etc. The *kinetic stability* of the metal ion-polymer crosslinking complex also has been shown to influence directly the physical (rheological) properties of a gel.⁵⁻¹⁰

The vast majority of the studies on, and applications of, metal ion crosslinked polymer gels have employed polymers bearing reactive alcohol or carboxylate functional groups.¹⁻³ In view of the foregoing considerations, this limited range of metal-binding functional groups implies inherent limits to the range of chemical and physical gel properties that can be achieved. To the best of our knowledge, previous studies have not addressed the possibility of tailoring the conditions for gelation and the physical properties of metal ion-polymer gels through the incorporation of specific metal-ligating functional groups into the polymer.

In the present paper we describe the preparation of acrylamide co-polymers bearing small amounts of co-monomers that possess particular metal-ligating characteristics.¹¹ The presence of these functional groups is shown to alter significantly and, to a degree, predictably the conditions for gel formation in the presence of metal ions with respect to the traditional polymers. The new crosslinking chemistry is also shown to have an influence on the rheological properties of the gels formed.

EXPERIMENTAL

Materials. The two commercial polyacrylamides employed in this study were obtained from Aldrich (cat. 18,127-7; <0.5% hydrolyzed by ¹³C NMR; nominal mw 5-6 × 10⁶ g/mol) and Lamberti (Lamflood 0175, 4.2% hydrolyzed, mw 5.7 × 10⁶ g/mol determined by viscometry). The HPG (Lamgum) was obtained from Lamberti and used without further purification. Other chemicals were obtained from standard commercial sources or prepared as described below. Acrylamide monomer was purified by double recrystallization with chloroform, potassium persulfate by double recrystallization from water.

Monomer Syntheses

Ligating co-monomers containing the acrylamide polymerizable group were obtained by the reaction of acryloyl chloride with the appropriate amine or imine derivative of the ligand. Where not commercially available, these were prepared as described below. A representative synthesis of the ligating acrylamide co-monomers is given below for acrylamidodiacetic acid.

Acrylamidodiacetic acid (AMD). To 420 mL of a solution of 16g (0.12 mol) iminodiacetic acid 0.2 N in NaOH was added 30.8 g (0.342 mol) acryloyl chloride at 0°C. After 2 h at 0°C the solution was extracted with ethyl acetate to remove unreacted acid chloride. The aqueous phase was passed through a cation exchange resin (Dowex 50X8) to convert the product to the acid form and eliminate excess NaOH. The product-containing fractions were found to contain about 20% of a byproduct. Purification of the desired product was effected by high pressure liquid

chromatography, HPLC, on reversed phase RP18 silica gel with a 90:10 water:methanol mixture containing 2% trifluoroacetic acid as eluent.

4-Acrylamido salicylic acid (AMS). The above procedure was followed with the following modifications: An equimolar ratio of 4-amino salicylic acid and acryloyl chloride were used. The reaction mixture was warmed to ambient temperature after the addition and allowed to react for 2 h followed by extraction of the product with CH_2Cl_2 in order to eliminate unreacted acryloyl chloride. After acidification to pH 4 with HCl the product was extracted with ethyl acetate. The resulting solution was dried over Na_2SO_4 and concentrated under rotary evaporation. Treatment with ethyl ether led to the precipitation of the white product which was isolated by filtration in 45% yield.

3-Acrylamido phthalic acid (3-AMP). 3-Amino phthalic acid was obtained by reduction of 3-nitro phthalic acid with H_2 in the presence of PtO_2 as described in the literature.¹² The synthesis of the acrylamide derivative followed the general procedure. After acidification of the ethyl acetate-extracted reaction mixture the product separated on standing at 0°C and was isolated in 92% yield by filtration followed by a THF rinse and drying under vacuum.

4-Acrylamido phthalic acid (4-AMP). This product was prepared starting from 3-nitro salicylic acid following the same procedure given above for 3-AMP.

2-Acrylamido malonic acid (AMM). This monomer was prepared from 2-amino diethylmalonate using the standard procedure with the following modifications: The addition was carried out at 5°C after which the solution was allowed to react at ambient temperature for 1 h. The product was converted to the acid form on a Dowex 50X8 cationic exchange column. The product-containing fractions were lyophilized to give the desired product in 87% yield.

2-Allyl malonic acid (ALM). To a suspension of 32g (0.2 mol) diethylmalonate and 65g of the basic resin Amberlite IRA400 (approx. 0.5 mol in hydroxide) in 400 mL anhydrous ethyl alcohol were added 24.2g (0.2 mol) allyl bromide. After allowing 2 h for reaction the resin was separated by filtration and the filtrate concentrated and then chromatographed on a silica gel (Merck Lobar Si60) column with 95:5 hexane:ethyl acetate as eluent. The 19g of 2-allyl diethylmalonate thus obtained were treated with 20% NaOH for 2 h yielding the desired ALM as its sodium salt.

N-allyl iminodiacetic acid (ALD). To a solution of 10g (0.075 mol) of iminodiacetic acid in 100 mL 2 N NaOH were added 6.05 (0.05 mol) allyl bromide. The mixture was left to react for 3 h at 40°C and then extracted with ethyl acetate to eliminate the unreacted allyl bromide. The aqueous phase was acidified to pH 3.5, concentrated, and isolated by HPLC on a reversed-phase silica gel column (RP18) with water as eluent.

All monomers prepared gave the expected ^1H NMR spectra, and were substantially free of impurities. Additional characterization by IR or mass spectrometry was carried out on several samples.

Co-polymer syntheses

Poly(acrylamide-co-4-acrylamido salicylic acid), P(AAm-AMS). To a reaction flask fitted with a mechanical stirrer and condenser were introduced 200 mL deionized water, acrylamide (20 g, 0.282 mol) and AMS (1.81 g, 0.0087 mol, molar ratio AAm/AMS = 97/3), after which the pH was adjusted to 9 with 2 N NaOH. The solution was de-aerated with a nitrogen purge for 2 h, heated to 60°C, and a solution of 4,4'-azobis(isobutyronitrile) (AIBN, 23.8 mg, 0.145 mmol) in 5 mL tetrahydrofuran (THF) was added quickly. After 2.5 h at 60°C the polymer was isolated by means of precipitation (repeated twice) at pH > 10 with methanol. After drying under vacuum, 20.3 g of polymer were obtained.

Poly(acrylamide-co-2-allyl malonic acid), P(AAm-ALM). To a 100 mL reaction vessel fitted with mechanical stirrer and condenser were introduced 30 mL deionized water, acrylamide (2.5 g, 0.035 mol), and the monomer ALM (0.52 g, 0.0036 mol, molar ratio AAm/ALM = 90/10) after which the pH was adjusted to 7 with 2 N NaOH. After de-aerating for 2 h with a nitrogen purge, solid potassium persulfate (10.4 mg, 0.00386 mmol) was added and the mixture was heated to 60°C for 2.5 h. After cooling, 2.95 g of the polymer were isolated as described for P(AAm-AMS).

Poly(acrylamide-co-acrylimido diacetic acid) P(AAm-AMD). To a 500 mL reaction flask fitted with a mechanical stirrer and condenser were introduced 200 mL deionized water, acrylamide, (20 g, 0.282 mol) and AMD (1.63 g, 0.0087 mol, molar ratio AAm/AMD 97/3), after which the pH was adjusted to 9 with 2 N NaOH. The solution was de-aerated with a nitrogen purge for 2 h, heated to 60°C and a solution of potassium persulfate (78.4 mg, 0.29 mmol) in 5 mL water was added quickly. After 1.5 h at 60°C the polymer was isolated by means of precipitation (repeated twice) at pH > 10 with methanol. After drying under vacuum, 21.3 g of polymer were obtained.

Poly(acrylamide-co-2-acrylamido malonic acid), P(AAm-AMM). The polymer was prepared with the same procedure employed for the preparation of P(AAm-AMD), employing 1.5 g (0.0087 mol, molar ratio AAm/AMM = 97/3) AMM in substitution of the AMD co-monomer, and reducing the reaction time to 1.25 h.

Poly(acrylamide-co-3-acrylamido-o-phthalic acid), P(AAm-3-AMP). The copolymerization followed the procedure described above for P(AAm-AMD) employing 2.1 g (0.0087 mol, molar ratio AAm/3-AMP = 97/3) 3-AMP as co-monomer.

Poly(acrylamide-co-4-acrylamido-o-phthalic acid), P(AAm-4-AMP). The copolymerization followed the procedure described above for P(AAm-3-AMP), employing 3.4 g (0.0145 mol, molar ratio AAm/4-AMP = 95/5) 4-AMP as co-monomer and increasing the reaction time to 2.5 h.

Poly(acrylamide-co-N-acrylamido glycolic acid), P(AAm-AMG). This polymer was obtained by means of the derivatization of a substantially unhydrolyzed commercial PAAm of mw 5–6 × 10⁶ g/mol: To 15 g (0.21 mol) of PAAm dissolved in 500 mL deionized water were added over 20 minutes with continuous stirring

TABLE I
Ligating acrylamide co-polymers prepared

Functionalized co-monomer	Co-monomer abbreviation	Mol. % ligating co-monomer	Co-polymer molecular weight* (x 10 ⁶ g/mol)
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CO} \\ \\ \text{HN}-\text{CHCO}_2\text{H} \end{array}$	AMG	1.2	5.6
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CO} \\ \\ \text{HN} \\ \\ \text{C}_6\text{H}_3(\text{OH})(\text{CO}_2\text{H}) \end{array}$	AMS	2.6	1.9
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CO} \\ \\ \text{HN}(\text{CH}_2\text{CO}_2\text{H})_2 \end{array}$	AMD	2.7	5.7
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CO} \\ \\ \text{HNCH}(\text{CO}_2\text{H})_2 \end{array}$	AMM	2.9	3.4
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CH}_2-\text{N}(\text{CH}_2\text{CO}_2\text{H})_2 \end{array}$	ALD	0.7	7.4
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CH}_2-\text{CH}(\text{CO}_2\text{H})_2 \end{array}$	ALM	4.5	1.3
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CO} \\ \\ \text{HN} \\ \\ \text{C}_6\text{H}_3(\text{CO}_2\text{H})_2 \end{array}$	4-AMP	4	3.2
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CO} \\ \\ \text{HN} \\ \\ \text{C}_6\text{H}_3(\text{CO}_2\text{H})_2 \end{array}$	3-AMP	3	3.7

- * Mw by GPC determination except for AMG co-polymer, which was prepared by derivatization of a commercial PAAm (declared mw 5-6x10⁶ g/mol).

3.89 g (0.042 mol) glyoxylic acid monohydrate in 250 mL deionized water basified to pH 10.3 with 2 N NaOH. The reaction mixture was then heated to 60°C for 2 h. The usual precipitation procedure was employed to obtain the polymer, 1.2% functionalized with glycolic acid.

Poly(acrylamide-co-N-allyl iminodiacetic acid), P(AAm-ALD). To a 100 mL reaction vessel were introduced 50 mL deionized water, acrylamide (8.5 g, 0.1197 mol) and ALD (4.5 g, 0.0063 mol, molar ratio AAm/ALD = 85/5) and the pH was adjusted to 4 with 0.5 N NaOH. After 30 min de-aeration with a nitrogen purge, 5.5 mg AIBN were added and the solution was heated to 50°C for 3.25 h. The usual polymer precipitation afforded 2.77 g of polymer.

Co-polymer compositions were determined by ^{13}C NMR on their aqueous solutions containing about 10% of the dissolved co-polymer. On account of the high polymer concentrations (necessary in order to have acceptable analysis times) the solutions were for the most part quite viscous and the resulting spectra gave rise to notably broadened resonances. Estimates of the mol% ligating co-monomer were determined by comparison of the carbonyl carbons of the acrylamide co-monomer and the ligating groups. These data were in good agreement with the co-polymer compositions calculated from the C/N weight ratios from elemental analysis. In no case was the presence of the acrylate group detected in the NMR spectra (limit of detection <0.5 mol%).

Co-polymer molecular weights were determined by GPC with 3 Shodex OH columns (one B-805 and two B-806) and referenced to 4 commercial PAAm molecular weight standards (Polysciences) covering the range from $0.6\text{--}9 \times 10^6$ g/mole. Solutions of the polymers 0.05 wt% were prepared in aqueous KCl (0.2 M KCl) and allowed to age for one week under mild agitation in order to reach a stable hydrodynamic volume.

Co-polymer structures, compositions and molecular weights are given in Table 1.

Preparation of gels. Our procedures for the preparation of Cr^{+3} gels have been described previously.¹³ In the present study the Cr^{+3} /co-polymer solutions were allowed to gel at 60°C.

After leaving the gels to equilibrate for one month or more at ambient temperature the rheological properties of Cr^{+3} /co-polymer gels prepared with initial pH 5 were determined over the frequency range 0.001–10 at 25°C on a Bohlin VOR rheometer using a cone-and-plate geometry. All gels had remained within 0.5 pH units of the initial pH (5). The G' values were not exactly constant over the measured frequency range, but increased from 4 to 8 Pa with increasing frequency. Average values are reported in Table II.

The B^{+3} gels described in Table III were prepared with $\text{Na}_2\text{B}_4\text{O}_7(10\text{H}_2\text{O})$ by a procedure similar to that for the Cr^{+3} gels except that the crosslinking reaction, where it occurred, was instantaneous. In order to assure relatively homogeneous mixing of the polymer and crosslinker, the solutions were vigorously agitated mechanically for a minute or so, and then left to equilibrate for several hours at 60°C. Rheological measurements were carried out on gels further equilibrated for several days at 25°C. Gel compositions prepared with HPG (5000 ppm) were 350 ppm in B^{+3} , with P(AAm-AMS) (12000 ppm) 1800 ppm in B^{+3} , and with P(AAm-AMG) (12000 ppm) 1350 ppm in B^{+3} . Both distilled water and 0.5 M NaCl solutions were employed to prepare the gels.

TABLE II
Aqueous ligating co-polymer gels prepared with Cr^{+3} ^a

Polymer	Mol. % ligating co-monomer	Maximum gelation pH	Storage modulus, G' , at pH 5 ^b (Pa)
PAAm	4.2 ^c	6.7	15
P(AAm-AMG)	1.2	8	56
P(AAm-AMS)	2.6	9	57
P(AAm-AMD)	2.7	7	56
P(AAm-AMM)	2.9	8	46
P(AAm-ALD)	0.7	8	53
P(AAm-ALM)	4.5	7.5	46
P(AAm-4-AMP)	4	7	54
P(AAm-3-AMP)	3	7	48

^aAll compositions 8000 ppm in polymer, 100 ppm in Cr^{+3} except that employing P(AAm-AMS) (15000 ppm polymer).

^bAverage G' value in the plateau region.

^cRefers to mol% acrylate groups in the polymer; PAAm mw 5.7×10^6 by viscosity analysis.

RESULTS AND DISCUSSION

An examination of the coordination chemical literature for Cr^{+3} , presently the most important metal ion crosslinker in gels applied for EOR, led to the targeting of dicarboxylate and hydroxy carboxylate ligating groups for incorporation into a water soluble polymer. The hydroxy carboxylate groups were also expected to display significant binding activity toward B^{+3} , the most widely employed cross-linking ion for gels applied in reservoir fracturing.

Acrylamide was selected as the most attractive co-monomer on the basis of its excellent co-polymerization characteristics and the well-characterized properties of its polymer solutions and gels. Our synthetic strategy focused on the incorporation of the functional groups into polymerizable vinylic co-monomers. Of the seven ligating co-monomers prepared (Table I), five were N-substituted acrylamide derivatives, and two were simple ethylenic derivatives. The most convenient route

TABLE III
Aqueous ligating co-polymer gels with B⁺³

Polymer	pH range for gelation
PVA, HPG	> 7.5
PAAm (4.2% hydrolyzed)	a
P(AAm-AMS)	1.3-3.5
P(AAm-AMG)	1.5-3.2
P(AAm-AMD)	a
P(AAm-AMM)	a
P(AAm-ALD)	a
P(AAm-ALM)	a
P(AAm-4-AMP)	a
P(AAm-3-AMP)	a

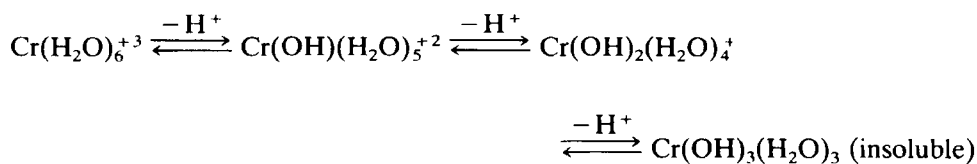
^aNo gelation detected over a wide pH range.

to the glycolic acid-functionalized co-polymer P(AAm-AMG) proved to be via derivatization of PAAm polymer with glyoxalic acid.

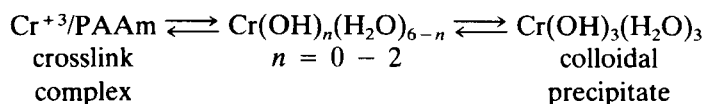
The co-monomer syntheses and co-polymerization reactions with acrylamide presented no particular difficulties; the principal characteristics of the ligating co-polymers prepared are given in Table I. The gelation chemistry of aqueous solutions of these co-polymers with Cr⁺³ and B⁺³ ions is described below.

Cr⁺³ crosslinked gels

The principal features of the aqueous solution chemistry of Cr⁺³ are summarized in the equation below:



The hexahydrate of Cr^{+3} predominates at low pH ($\text{pH} < 3$), but rapidly equilibrates with the mono-, di- and trihydroxides at higher pH.¹⁴ The trihydroxide, which forms to a measurable extent above pH 5.5, is extremely insoluble in aqueous solution and recent work has established that it is unreactive toward PAAm cross-linking.¹⁵ At pH 6 the solubility limit of Cr^{+3} [as a mixture of the species $\text{Cr}(\text{OH})_n(\text{H}_2\text{O})_{6-n}$ ($n = 0-2$)] is only about 10 ppm.¹⁴ Nevertheless, aqueous solutions of Cr^{+3} and polyacrylamide (PAAm) gel as high as pH 7. We have presented evidence that gelation in the interval pH 6–7 occurs as the result of a shift to higher pH of the equilibrium for $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$ precipitation, driven by Cr^{+3} -polymer complexation^{4,15}:



As predicted on the basis of the equilibrium written, the upper pH limit for gelation is dependent on the degree of PAAm hydrolysis. Thus, whereas 1–2% hydrolyzed PAAm gels only at $\text{pH} \leq 6.7$, with 10% hydrolyzed PAAm gelation takes place as high as pH 7.0.

These observations suggested to us that the upper pH limit for gelation of Cr^{+3} /polymer solutions can provide a useful indication of the relative thermodynamic strength of the Cr^{+3} -polymer crosslinking complexes formed (assuming equal concentrations of Cr^{+3} and polymer functional groups). Upper pH limits for gelation of the 8 ligating co-polymers prepared in the present study are given in Table II, along with that for a comparably functionalized PAAm (4.2% hydrolyzed, $5-6 \times 10^6$ mw). Five of the co-polymers formed firm gels with Cr^{+3} to a pH significantly higher than the hydrolyzed PAAm reference. On the other hand, the acrylamide co-polymers with AMD and 3- and 4-AMP gave firm gels only to pH 7, which is only modestly superior to that of the partially hydrolyzed PAAm reference.

Cr^{+3} gels prepared with the reference PAAm are markedly turbid above pH 6.5, reflecting the presence in the solution or gels of a discrete proportion of the Cr^{+3} as $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$. The Cr^{+3} gels prepared with the AMG, AMS, AMM, and AMD co-polymers were transparent to pH 7 or beyond, consistent with the hypothesized shift in the equilibrium for $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$ precipitation.

The rheological properties of these gels have also been examined in order to determine the influence of the modified crosslinking chemistry on their physical properties. The theory of rubber elasticity predicts a linear dependence of the storage modulus, G' , in the plateau region on the number of crosslinks in a polymeric network.¹⁶ Assuming that in Cr^{+3} crosslinked PAAm a significant fraction of the Cr^{+3} remains un-bound or singly-bound to the polymer at equilibrium, we would expect an increase in the equilibrium constant for metal ion-polymer complexation to produce an increase in the number of crosslinks and hence in G' for a given concentration of polymer and metal ion.

Whereas the storage modulus for the reference Cr^{+3} /PAAm gel, which bears the monocarboxylate (acrylate) functional group of moderate Cr^{+3} ligating ability,¹⁷

was 15 Pa, under the same conditions the ligating co-polymer gels all had G' values between 46 and 57 Pa (Table II). Of course, a number of factors such as the polymer molecular weight, conformation, rigidity, or electrostatic charge can influence the G' values for a polymer gel. Nevertheless, in view of the facts that: (1) the PAAm and the AMG, AMD, AMM, and ALD co-polymers studied were of similar molecular weight, and (2) the PAAm had a higher degree of functionalization (2–4 times) than these co-polymers, we assign the increased storage moduli of the ligating co-polymer gels to an increased thermodynamic driving force for formation of the crosslinking complexes.

Over the pH range 7–9, the initially firm $\text{Cr}^{+3}/\text{P}(\text{AAm-AMS})$ gels reverted spontaneously to fluid solutions after a week at 60°C. In contrast, the same polymer gels prepared at lower pH were stable for more than 6 weeks at the same temperature. These observations were confirmed in duplicate experiments. We have not further analyzed this result, but we note in passing that similar behavior has been reported for a Fe^{+3} -crosslinked polymer gel.¹⁸ For the Fe^{+3} gels, de-gelation was attributed to spontaneous reversion of less stable intermolecular crosslinking complexes to more stable, but unproductive, intramolecular crosslinks.

B^{+3} crosslinked gels

Hydroxyl-functional synthetic and biopolymer gels crosslinked with B^{+3} are well known, and are of considerable importance in the petroleum industry for reservoir fracturing applications.² These gels form above pH 7.5, the pH range over which the diol-complexing ion $\text{B}(\text{OH})_4^-$ is formed to a significant extent in aqueous solution.¹⁹ The $\text{B}^{+3}/\text{polyol}$ gels are characterized by marked thermal reversibility, reflecting the facile B^{+3} -polymer dissociation reaction.^{5,7,9,10,20}

In contrast, acrylate functional polymers such as partially hydrolyzed PAAm do not gel in the presence of B^{+3} ion in aqueous solution at any pH. This behavior is explained by considering that monomeric $\text{B}(\text{carboxylate})_2$ complexes are thermodynamically unstable with regard to hydrolysis.^{21,22} $\text{B}(\text{dicarboxylate})$ complexes are similarly unstable in aqueous solution.²¹ In contrast, significant binding constants are found for the reaction of B^{+3} with alpha-hydroxy acids to form $\text{B}(\text{alpha-hydroxy carboxylate})$ complexes.²¹

On the basis of these considerations, we expected the hydroxy acid-functional ligating co-polymers to be good candidates for gelation with B^{+3} under conditions of acid pH. This prediction was confirmed (Table III), with the $\text{P}(\text{AAm-AMG})$ and $\text{P}(\text{AAm-AMS})$ co-polymers forming B^{+3} gels below pH 3.5 and 3.2, respectively. The contrast with the pH range for B^{+3} gelation of polyols is striking. Further, whereas B^{+3} does not crosslink PAAm itself in water, the presence of only 1–3% hydroxy acid functional groups is sufficient to render PAAm crosslinkable. As expected, no gels were formed with the dicarboxylate functionalized PAAm co-polymers.

The formation constants of 1:2 B^{+3} complexes with alpha-hydroxy carboxylates are greatest at a pH near the pK_a value of the hydroxy acid,²¹ which typically are below about pH 4. The gelation pH range found for the ligating co-polymers $\text{P}(\text{AAm-AMG})$ and $\text{P}(\text{AAm-AMS})$ are somewhat lower than the pK_a values of the parent glycolic and succinic acids (pK_a 3.8 and 3.0, respectively). However,

when allowance is made for the electron withdrawing inductive effect of the amide substituent, the observed gelation ranges are in quite satisfactory agreement with the prediction.

As noted above, B^{+3} /polyol gels are characterized by their facile thermal reversibility. This reversibility, in fact, poses an upper temperature limit on their applications in reservoir fracturing, and provides a stimulus for the development of polymer gels that maintain their physical properties over a wider temperature range. The crosslink reversibility is evidenced in a dynamic rheological experiment by a marked dependence of the storage modulus on the measurement frequency, as illustrated in Figure 1 for a B^{+3} /hydroxylpropyl guar (HPG) gel at 40°C.

Several physical-chemical studies have examined the relationship between the ligand exchange chemistry of the B^{+3} /polymer crosslinking complexes and the rheological properties of gels formed with polyvinyl alcohol,⁵ galactomannan,⁹ and HPG.^{7,10} The point of intersection of G' and the loss modulus, G'' , essentially defines the observation timescale over which the elastic or fluid properties of the gel will predominate: below the G'/G'' intersection frequency the composition will behave as a fluid and above it, as an elastic solid. The movement of this intersection point to higher frequency with increasing temperature has been correlated with the increased rate of ligand exchange in B^{+3} /HPG gels.⁷

The dynamic rheological properties of the two B^{+3} /ligating co-polymer gels with P(AAm-AMG) and P(AAm-AMS) have been examined over the temperature range 5–75°C. Figure 2 shows the dynamic moduli at 25°C and 75°C for a B^{+3} /P(AAm-AMS) gel prepared at pH 3.4. In marked contrast to B^{+3} /HPG gels, the B^{+3} /P(AAm-AMS) gel at 25°C displays the rheological characteristics of a permanently cross-linked network. Of course, the G' and G'' values would be expected to intersect at a sufficiently low, but inaccessible, frequency even at this temperature. Only at 75°C does the G'/G'' crossover appear in the rheogram.

On the other hand, a B^{+3} /P(AAm-AMG) co-polymer gel prepared at pH 1.5 in

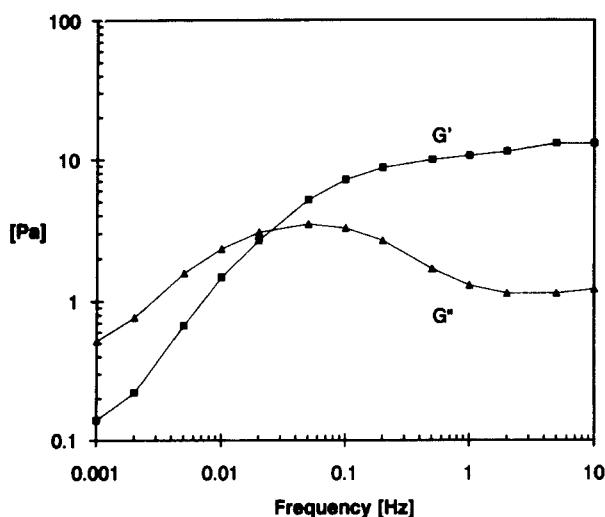


FIGURE 1 Storage (G') and loss (G'') moduli of B^{+3} /HPG gel at 40°C as a function of frequency.

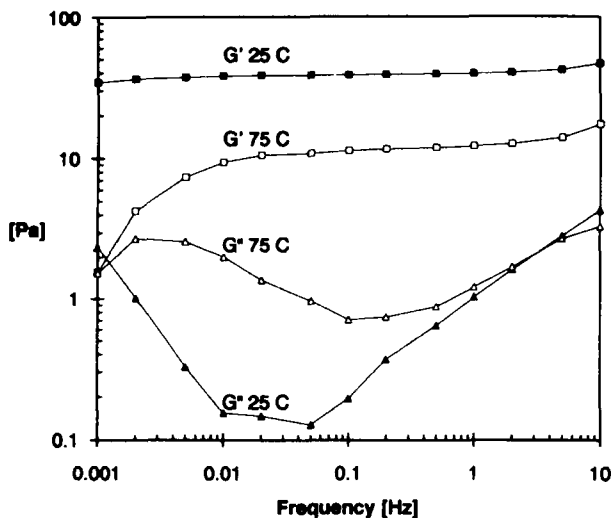


FIGURE 2 Dynamic moduli of $B^{+3}/P(\text{AAm-AMS})$ gel (pH 3.4) at 25° and 75°C.

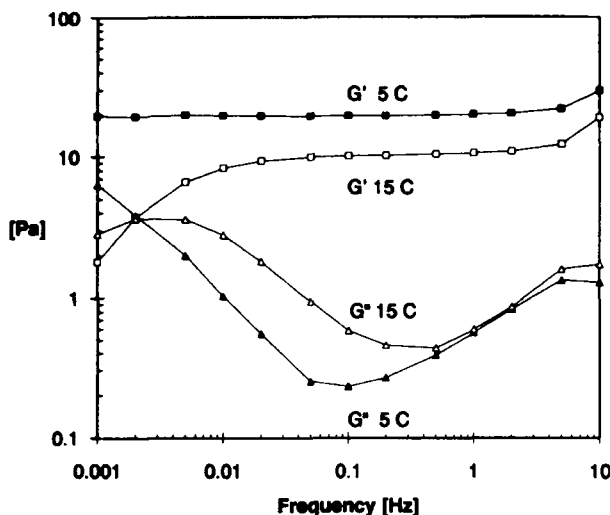


FIGURE 3 Dynamic moduli of $B^{+3}/P(\text{AAm-AMG})$ gel (pH 1.5) at 5° and 15°C.

0.5 M NaCl displays marked reversibility already at 15°C and resembles qualitatively the $B^{+3}/P(\text{AAm-AMS})$ co-polymer gel at 75°C (Figure 3). In fact, only at 5°C does the $B^{+3}/P(\text{AAm-AMG})$ gel behave as a permanent network from the point of view of the rheological measurement.

These results strongly imply that the kinetic stability of the crosslinking complexes formed in the $B^{+3}/P(\text{AAm-AMS})$ gel is much greater than those in the $B^{+3}/P(\text{AAm-AMG})$ gel. The absence of data on the kinetic stabilities of the corresponding $B^{+3}/\text{monomer}$ complexes in the literature precludes an independent evaluation of these results. The role of pH and salinity still must be examined in order to achieve a full characterization of the rheological properties of these gels.

Nevertheless, the results clearly demonstrate that the goal of chemically modifying the thermal reversibility of metal ion crosslinked polymer gels through the incorporation of specific ligating functional co-monomers has been achieved. It is also of potential technological interest that the $B^{+3}/P(AAm-AMS)$ gel retains its elastic properties to significantly higher temperature than $B^{+3}/$ polyvinyl alcohol or B^{+3}/HPG gels, in view of the wide applications of the latter in the petroleum industry.^{1,2}

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