Kinetics of the Cross-Linking of Polyacrylamide with Cr(III). Analysis of Possible Mechanisms

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The reaction between chromium(III) and partially hydrolyzed polyacrylamide (HPAM) has been investigated by UV−visible spectroscopy. We found that the reaction between Cr(III) and HPAM can show a biphasic response. Initial rate experiments show saturation kinetics. The influence of reactant concentrations on the kinetics has been studied, and possible mechanisms consistent with the experimentally observed kinetic behavior have been derived.

Introduction

Chromium(III)−polyacrylamide (HPAM) systems can be used for polymer gel treatment in enhanced oil recovery.[1] In these systems, Cr(III) acts as a cross-linker, forming polymeric aggregates with high viscosity which finally block pores in the reservoir. The cross-linking process is assumed to consist of a complexation between Cr(III) ions and carboxylate groups from hydrolyzed amide groups on the polymer.

The effects of pH, temperature, and reactant concentrations in these polymer gels have previously been studied by visual inspection of gelation times[1,2] or by use of rheological methods.[3] Kinetic investigations of similar systems using equilibrium dialysis[4] and NMR spectroscopy[5] have also been performed.

In this paper we report the results of a kinetic study where the reaction between Cr(III) and HPAM has been investigated by UV−visible spectroscopy. In general, this method can provide information on the interaction between a transition metal cation and coordinated ligands.[6] UV−visible spectroscopy has also been used in the study of reactions between Cr(III) and a variety of organic substrates.[7−9]

We found that the reaction between Cr(III) and HPAM under certain conditions shows a biphasic response. Double-reciprocal plots between initial velocities of this process and initial HPAM concentrations are found to be linear. Mechanisms consistent with the biphasic behavior and double-reciprocal plots have been derived.

Materials and Methods

Polymer Solutions. Partially hydrolyzed polyacrylamide "Alcoflood 254" supplied by Allied Colloid (U.K.) with an average molecular weight of 500 000 and an approximately 5% degree of hydrolysis was used in the experiments. A stock solution of polyacrylamide in 0.5 M NaCl was prepared. The solution was stirred rigorously on a magnetic stirrer for 2 days. The polymer was further hydrolyzed by the addition of NaOH, giving a final base concentration of 0.1 M, which was neutralized by addition of concentrated HCl after approximately 1 day. The polymer solution was filtered through Millipore MF membrane filters down to 0.65 mm. Before filtration the solution was turbid; this turbidity disappeared with filtration. Carboxylate group concentration and hence also the degree of hydrolysis were determined by titrimetric analysis. Two different polyacrylamide solutions prepared in the same manner were used in the experiments. For determination of pseudo-first-order rate constants a polyacrylamide solution of 30 g/L was prepared. The hydrolysis procedure above gave a polymer solution with approximately 150 mM acid groups and a degree of hydrolysis of 36%. The initial rate experiments were performed using a polymer standard solution of 20 g/L with 55 mM acid groups and a 20% degree of hydrolysis.

Reaction Mixtures. A reaction mixture (20 mL) was prepared in a vial tube for each experiment. Polymer stock solution and 0.5 M NaCl and NaOH in the required amounts to give reaction mixtures of desired pH were thermostated in a water bath. The reaction was started by the addition of Cr-(NO₃)₃. Cr(NO₃)₃ stock solutions were stored in 0.5 M hydrochloric acid in order to prevent the formation of polymeric Cr(III) species.[10]

Concentrated polyacrylamide solutions scatter light considerably, making them not useful for spectrophotometric measurements. Polymer concentrations in the range 27−81 mM in polyacrylamide, corresponding to 6−16 g/L have been used for the determination of pseudo-first-order constants. In the initial rate experiments polymer carboxylate concentrations of 2.7−38 mM corresponding to 1−13 g/L have been used.

Instrumentation. Spectrophotometric measurements were performed on a Hitachi U-2000 spectrophotometer. The spectrophotometer was connected with an IBM compatible PC for data acquisition. For measurements in the visible part of the spectrum, glass cells with a 5 cm light path were used. The pH values of the reaction mixtures were measured with a Radiometer GK2401 pH electrode. Rheological measurements were performed on a Bohlin CS10 controlled stress rheometer.

Results

Spectra. The spectra of Cr(III) complexes are well understood in their main features.[11] There are three expected allowed transitions, and these have been observed in a considerable number of complexes. In octahedral Cr(III)−aqua complexes, the bands are found at 17 400, 24 000, and 37 000 cm⁻¹.[11] Figure 1 shows two of these absorption bands for Cr(III) ions in contact with HPAM as a function of time. The figure shows that during the reaction between Cr(III) and HPAM the UV−visible spectrum shows an increasing absorbance. The wavelength to study the kinetics of the reaction was chosen as 570 nm.
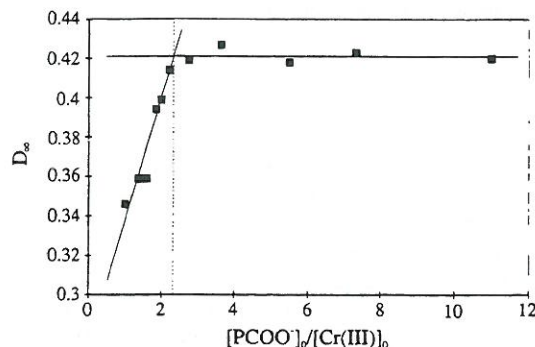
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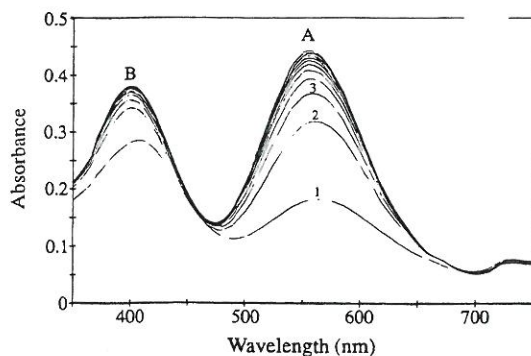
Figure 1. Spectrum of 2 mM Cr(III) and 15 mM HPAM (carboxyl groups) at 26 °C, pH 5.0: (1) initial spectrum of Cr(III) and HPAM, directly after mixing; (2, 3, ...) other spectra taken with 2 h intervals.


Figure 2. Final absorbance, D_∞, as a function of the initial molar ratio of HPAM carboxylate groups to Cr(III) for 2 mM Cr(III) at room temperature and pH 5.2. The stoichiometry is determined from the interaction of the solid lines fitted to the data points.

It has been suggested that a shoulder in the UV region at 264 nm can be used in the monitoring of the Cr(III)−HPAM reaction.[7] Under the experimental conditions for our experiments, this shoulder, although present, has not been found suitable for quantitative measurements. This is probably due to scattering effects which are more dominant at lower wavelengths (scattering is proportional to $1/\lambda^4$) and may result in greater errors.

Stoichiometry. The stoichiometry of the Cr(III)−HPAM reaction has been investigated by varying the initial HPAM/ Cr(III) ratio at constant Cr(III) concentration[12] and measuring the absorbance at 570 nm after equilibrium was established. Figure 2 shows the variation in the final absorbance, D_∞, at 570 nm as a function of the [PCOO⁻]₀/[Cr(III)]₀ ratio. We found that the molar ratio of HPAM carboxylate groups to Cr(III) is approximately 2.3:1. This supports a mechanism where one Cr(III) interacts with two carboxylic groups, similar to the one proposed by Lockhart et al.[13] In Figure 2 there is a break point from the region where D_∞ increases with the [PCOO⁻]₀/[Cr-(III)]₀ ratio to the region where a constant value of D_∞ is reached. This sharp break point is an indication of the irreversibility of the total reaction.

Kinetics. Curve A in Figure 3 shows a typical increase of absorbance as a function of time. Curve B shows $\ln(D_\infty - D_t)$ versus time, where D_∞ has been determined after 24 h. Biphasic first-order kinetics are observed, and from the semilog plot, curve B pseudo-first-order rate constants for phases I and II can be determined. Curve C is obtained by a linear regression of the $\ln(D_\infty - D_t)$ versus time data in the interval 3600−7200 s. After the influence of phase II on the $\ln(D_\infty - D_t)$ versus time plot is subtracted, phase I can be determined. Curve D is obtained by a linear regression of $\ln(D_\infty - D_t - \beta e^{-k_{II}t})$ versus
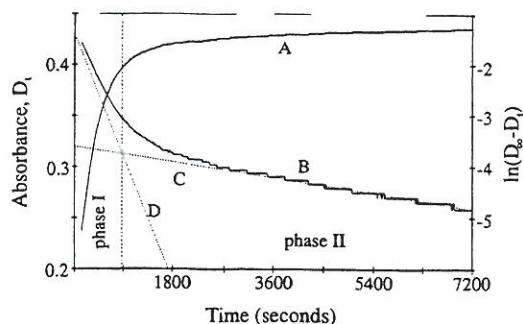
Figure 3. Curve A: absorbance, D_t, at 570 nm versus time for a reaction mixture of 2 mM Cr(III) and 30 mM HPAM carboxylic groups, pH 5.2. The tangent line indicates the "initial" velocity v_0. Curve B: $\ln(D_\infty - D_t)$ versus time. $D_\infty = 0.444$. Curve C: linear regression for phase II. Curve D: linear regression for phase I after subtracting the influence of phase II.
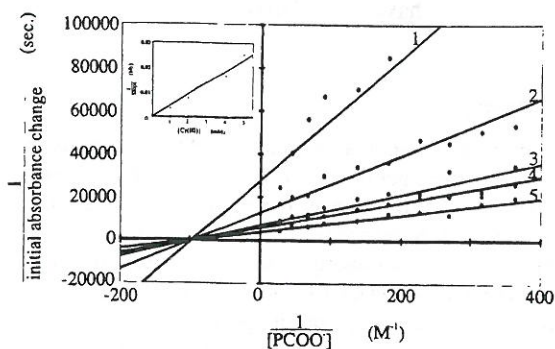
Figure 4. Double-reciprocal plots of initial absorbance changes for the Cr(III)−HPAM reaction. Numbers indicate the amount of Cr(III) in mM. For each Cr(III) concentration, HPAM concentrations are in the range 2.7−38 mM. Inset: secondary plot of the inverse slope of the double-reciprocal plot against Cr(III) concentration. The slopes are those obtained by forcing the solid lines to intersect in one point.

time data, where k_{II} is the rate constant of phase II determined from the slope of curve C and $\ln(\beta)$ is the intercept of curve C.

The inaccuracy of determining D_∞ can be avoided by using Guggenheim's method,[14] i.e. comparing the absorbance at constant time differences, h. In this case a biphasic plot is also obtained by plotting $\ln(D_{t+h} - D_t)$ versus time. The transition between phases I and II is slightly delayed but not enough to determine the constants of phase I correctly without making corrections due to the influence of phase II. The determination of phase II is even more inaccurate, since the absorbance differences in this phase are very small. Therefore the method presented for curves C and D is preferred.

Biphasic kinetics between Cr(III) and HPAM have been observed for mixtures containing 2 mM Cr(III) and 30 mM HPAM (carboxylic groups) in pH and temperature ranges of 5−6 and 27−35 °C, respectively. At pH values lower than 5, the biphasic character of the semilogarithmic plot disappears, giving a good monophasic first-order curve fit.

Double-reciprocal plots of the initial rate of absorbance change versus HPAM concentration show good linearity (Figure 4) and indicate saturation kinetics with a Michaelis−Menten type of rate law for part I of the biphasic process (Figure 3). Solid lines in Figure 4 have been calculated by the method of least squares as proposed by Cornish-Bowden and Wharton.[15] The lines are very close to intersecting at the abscissa. Forcing linear regression lines through one intercept results in only marginally larger values of the square deviation. The inset in Figure 4 shows a "replot", i.e. the inverse of the slope of the double-reciprocal plots plotted against the initial Cr(III) concentrations.

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Both from the replot and directly from initial rate versus [Cr-(III) at constant [HPAM], we found reaction orders with respect to Cr(III) in the range 1.0–1.3. Assuming a reaction order of 1 with respect to Cr(III) and saturation kinetics for polyacrylamide, the initial rate v_0 can be expressed as

$$v_0 = \frac{k[PCOO^-]_0[Cr(III)]_0}{K + [PCOO^-]_0} \qquad (1)$$

In accordance with the proposed saturation kinetics, a reaction order with respect to PCOO$^-$ less than 1 has been found for the rate constant of phase I of the biphasic plot. For phase II of the biphasic response (Figure 3) no systematic influence of polyacrylamide concentration on the rate constant was found, while the reaction velocity with respect to initial Cr(III) concentration still seems to be first order.

Influence of Hydrogen Carbonate Ions. During the first experiments we found some of our data difficult to reproduce. The source of irreproducibility was found to be the NaOH solution (used to adjust pH) that contained dissolved carbonate. Allowing the NaOH solution to be in contact with air before use resulted in higher reaction rates than when using carbonate-free NaOH. Similarly, addition of sodium bicarbonate to the Cr(III)–HPAM reaction mixture gave a similar enhancement in reaction velocity. In fact, a recent report by Aronson et al.[16] shows that bicarbonate accelerates the formation of Cr(III)–EDTA and other chromium(III) complexes. Although we have been eliminating HCO_3^-/CO_3^{2-} in our studies, this factor should be taken into consideration when using fresh or sea water as solvent in oil field applications of Cr(III) cross-linked gel systems.

Additional Observations. Rheological measurements have been made on some of the reaction mixtures. It has been found that viscosity, elastic modulus, and phase angle do not change significantly during the reaction, indicating that the solutions are far from the gelation threshold.

Variation of pH during an experiment was found to have a major influence on the reaction velocities during the initial part of the biphasic response. We have therefore measured the pH development in reacting solutions. Although excess polymer carboxylic groups can be expected to buffer and maintain the pH at a reasonably constant value, we found that the pH is lowered during the reaction by about 0.05 pH units. This decrease in pH results in a decrease of the reaction rate by approximately 10% with negative first-order dependence on [H$^+$]. Unfortunately conventional buffers for the pH range of interest in this study contain groups, for example carboxylate groups, giving competitive complexation reactions with Cr(III) and have for this reason not been used.

For comparison the reactions of Cr(III) with excess malonate and acetate have been studied under conditions similar to those for the reaction with polyacrylamide. It has been found that the reaction with malonate under these conditions also shows biphasic pseudo-first-order kinetics.

Discussion

Possible Cr(III)–HPAM Structure. Figure 1 shows that there are only small changes in the location of the absorption maxima when the carboxy groups of hydrolyzed HPAM react with Cr(III). This indicates that the octahedral arrangement around the Cr(III) central atom is not significantly disturbed. Further, the stoichiometric analysis indicates that first one and later two water molecules are replaced by carboxylic groups. Figure 5 shows a possible structure of Cr(III)–cross-linked polyacrylamide.
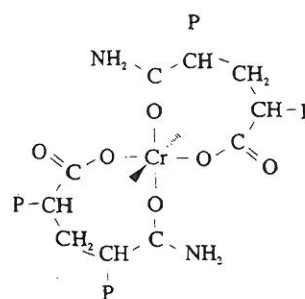

Figure 5. Proposed structure of the cross-link between Cr(III) ions and polyacrylamide.[2]

Possible Reaction Mechanisms. For a biphasic reaction the time dependent optical density will have the form

$$D_\infty - D_t = \alpha e^{-k_I t} + \beta e^{-k_{II} t} \qquad (2)$$

For both consecutive and parallel two-step reactions with reversibility in both steps, i.e. A $\rightleftharpoons$ B $\rightleftharpoons$ C, or A $\rightleftharpoons$ B and A $\rightleftharpoons$ C, the concentrations of the species are

$$[A] = [A]_0(c_{A1}e^{-k_I t} + c_{A2}e^{-k_{II} t} + c_{A3}) \qquad (3)$$

$$[B] = [B]_0(c_{B1}e^{-k_I t} = + c_{B2}e^{-k_{II} t} + c_{B3}) \qquad (4)$$

$$[C] = [C]_0(c_{C1}e^{-k_I t} + c_{C2}e^{-k_{II} t} + c_{C3}) \qquad (5)$$

The deduction of eqs 3–5 for consecutive and parallel mechanisms is presented in the supplementary material. The constants in these equations are functions of the rate constants of the system. The absorbance will be

$$D_t = \epsilon_A l[A] + \epsilon_B l[B] + \epsilon_C l[C] \qquad (6)$$

where ϵ_i is the molar absorptivity of component i and l is the cell path length. Inserting eqs 3–5 in eq 6 will give eq 2 with

$$\alpha = -[A]_0 l(\epsilon_A c_{A1} + \epsilon_B c_{B1} + \epsilon_C c_{C1})$$
$$\beta = -[A]_0 l(\epsilon_A c_{A2} + \epsilon_B c_{B2} + \epsilon_C c_{C2})$$
$$D_\infty = [A]_0 l(\epsilon_A c_{A3} + \epsilon_B c_{B3} + \epsilon_C c_{C3}) \qquad (7)$$

The values of the constants α and β depend on the molar absorptivities of the components and their initial concentrations. From eq 2 it can be seen that for certain rate constants and molar absorptivities a first-order semilogarithmic curve-fitting procedure can yield two linear regions from which k_I and k_{II} can be estimated. Because less absorption changes are taking place over a larger time period, the determination of k_{II} is subject to larger errors. The k_{II} value is also much more sensitive to errors in the determination of D_∞.

Biphasic first-order reaction kinetics can occur either with consecutive or with parallel first-order reactions. For consecutive processes the faster step observed in phase I can either be the first or the second reaction step. In the supplementary material optimized consecutive and parallel first-order schemes have been compiled that fit the experimental biphasic response shown in Figure 3. In the following we briefly describe the requirements to model the biphasic response of Figure 3 for each case.

When simulating these biphasic absorbance–time plots, the saturation behavior of the rate constant of phase I has not been taken into account. As a consequence of this the reaction order with respect to excess HPAM is estimated too high in these

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simulations. However, since the excess of HPAM is considered large enough compared to Cr(III), this overestimation is of little importance.

Mechanism with Consecutive Reactions. The appearance of Figure 2 indicates irreversibility of the overall reaction. A consecutive mechanism with an irreversible second step has therefore been simulated. Although there is an irreversibility in the total reaction, a reversible first step is possible and has been simulated.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \qquad (C1)$$

$$C + B \overset{k_2}{\rightarrow} D \qquad (C2)$$

In the scheme above reactant A is Cr(III), reactant B is HPAM, and the reaction products C and D are Cr(III) reacted with one and two HPAM chains. The reactions C1 and C2 are simulated as second-order reactions, but since the concentrations used in the experiment shown in Figure 3 also have been used when simulating, B is in excess and pseudo-first-order kinetics are observed.

It has been found that no fit to Figure 3 is possible when $K_1 = k_1/k_{-1} < 96$ M^{-1}. In the case where the first step is the faster, the absorptivity of C increases when K_1 decreases from ∞ (irreversible reaction) to 100. The absorptivity of C is on the same order of magnitude as the absorptivity of D determined from D_∞. In the case where C2 is the faster reaction, the biphasic behavior of Figure 3 requires an absorptivity of C that is almost 10 times higher than that of D. This seems unlikely, and therefore this case is discarded. A summary of the simulation results is given in the supplementary material.

Mechanism with an Additional Parallel Reaction. Another possible mechanism for the observed biphasic reaction consists of an irreversible consecutive reaction of A with two molecules of B, yielding D, with an addition parallel reversible reaction of A yielding E, i.e.

$$A + B \overset{k_1}{\rightarrow} C \qquad (P1)$$

$$C + B \overset{fast}{\longrightarrow} D \qquad (P2)$$

$$A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E \qquad (P3)$$

For the cross-linking of HPAM with Cr(III), A–D are defined as before. E is the reaction product of the parallel reaction. The above scheme is in accordance with the observed stoichiometry and irreversibility of the total reaction.

No biphasic solution is possible in the case where P3 is irreversible, and it has been found that the maximum value of $K_2 = k_2/k_{-2}$ that gives biphasic behavior is 3.5. Again there are two solutions, P1 faster than P3, and P3 faster than P1, both of which give plausible solutions in certain ranges of K_2.

A candidate for the first-order reaction of Cr(III) alone, eq P3, is not known. An additional parallel reaction instead of eq P3 could be a reversible reaction between Cr(III) and HPAM. This is represented as the mechanism of reactions P1, P2, and P3b.

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E \qquad (P3b)$$

This mechanism gives a biphasic solution in a manner similar to that for the first parallel mechanism presented above. In the region where the reverse of reaction P3b dominates phase II,

this mechanism also gives low polymer concentration dependency in this phase, as the experiments indicate. The reverse of eq P3b will be the rate determining step of phase II if reaction P1 is faster than reaction P3b but not if reaction P3b is faster than reaction P1.

A mechanism where the byproduct E does not reverse to A and B but forms C directly can give an absorbance–time plot similar to that for the mechanism above. That is, reaction P3 is replaced by the two reactions P3c and P4c:

$$A + B \overset{k_2}{\rightarrow} E \qquad (P3c)$$

$$E \overset{k_3}{\rightarrow} C \qquad (P4c)$$

This mechanism has also been simulated. Biphasic solutions have been achieved with reaction P4c as the rate-determining step of phase II. This is similar to the previous mechanism with k_3 (P4c) $\approx k_{-2}$ (P3b) and also equal values of k_1 and k_2.

To simulate dimerization of Cr(III) as a possible competitive reaction of the cross-linking reaction, eq P3 is replaced with a second-order dimerization of A (P3d):

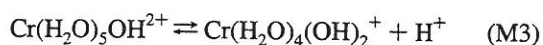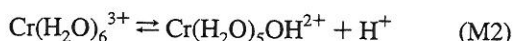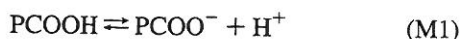$$2A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E \qquad (P3d)$$

The mechanism P1, P2, and P3c gives a good pseudo-first-order curve fit, even though eq P3d is a second-order reaction, only if eq P1 is the faster reaction observed in phase I. Then the reverse first-order reaction of eq P3d will be rate determining in phase II and linearity of the semilog plot will be observed in this phase too. Observations on Cr(III) solutions without polymer present seem to indicate that the absorptivity of the dimer is only slightly higher than twice the absorptivity of the Cr(III) monomer. The results of the simulations then give an approximate range of $K_2 = k_2/k_{-2}$ from 700 to 1000 M^{-1}. A summary of the simulation results is given in the supplementary material. However the value of K_2 is not in accordance with the stability constant of the Cr(III) dimer. Rotzinger et al.[10] have reported a stability constant of the dimer that is 2 orders of magnitude higher than the simulated value that gives the biphasic appearance of Figure 3. Data from the biphasic reaction with malonate have a rate constant for phase II which is much smaller than with HPAM. This also indicates that the chromium dimerization reaction or its reverse is not the reaction observed in phase II with both HPAM and malonate.

Proposed Mechanism for the Cr(III)–Polyacrylamide Reaction. For the faster reaction in the biphasic response, good first-order dependence with respect to Cr(III) concentration has been found both in the pseudo-first-order curve fit and for the initial rate experiments. The pseudo-first-order curve fit also indicates a first-order reaction in phase II, but as mentioned earlier there are larger experimental uncertainties in this phase of the reaction. A possible reaction mechanism consists of the binding of two HPAM chains to Cr(III) in two consecutive steps, as indicated from the observed stoichiometry. If the reaction proceeds by a consecutive mechanism, simulations have shown that the faster reaction of the biphasic plot is the binding of the first HPAM chain to Cr(III). Another possibility is an additional parallel reversible reaction between Cr(III) and HPAM. During phase II the reverse of this parallel reaction will be rate determining for the formation of cross-links between Cr(III) and HPAM.
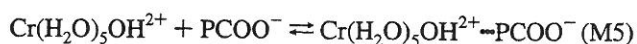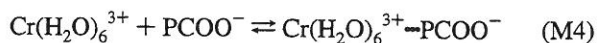
The occurrence of saturation kinetics for the first step might be due to an outer-sphere complex, as Tyagi and Khan[9] have reported for the Cr(III) acetate reaction. At pH 5–6 the

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hydrolyzed hexaaquochromium(III) ion is the dominating chromium species, thus giving the following mechanism
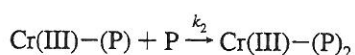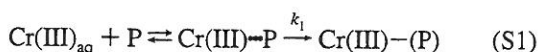
Acid−Base Equilibria:

$$PCOOH \rightleftharpoons PCOO^- + H^+ \qquad (M1)$$

$$Cr(H_2O)_6^{3+} \rightleftharpoons Cr(H_2O)_5OH^{2+} + H^+ \qquad (M2)$$

$$Cr(H_2O)_5OH^{2+} \rightleftharpoons Cr(H_2O)_4(OH)_2^+ + H^+ \qquad (M3)$$

Outer-Sphere Complex Formation:

$$Cr(H_2O)_6^{3+} + PCOO^- \rightleftharpoons Cr(H_2O)_6^{3+} \cdots PCOO^- \qquad (M4)$$

$$Cr(H_2O)_5OH^{2+} + PCOO^- \rightleftharpoons Cr(H_2O)_5OH^{2+} \cdots PCOO^- \qquad (M5)$$

Substitution of Water Ligands:

$$Cr(H_2O)_6^{3+} \cdots PCOO^- \xrightarrow{k_1} Cr(H_2O)_5(PCOO)^{2+} + H_2O \qquad (M6)$$

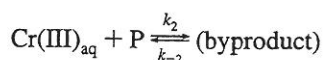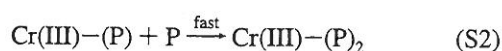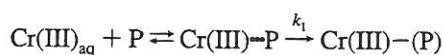$$Cr(H_2O)_5OH^{2+} \cdots PCOO^- \xrightarrow{k_{1'}} Cr(H_2O)_4(OH)(PCOO)^+ + H_2O \qquad (M7)$$
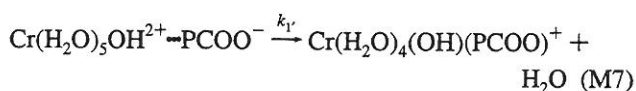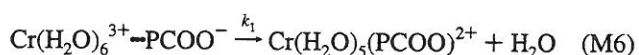
A description of the observed biphasic behavior must also include the reactions that incorporate the second carboxylic group in the coordination sphere of Cr(III). This process can occur after reactions M6 or M7, or by a sequence of processes where both carboxylic groups rapidly form an outer-sphere complex then followed by consecutive substitutions of water by PCOO⁻. The first of these alternatives can be formulated by the following skeleton mechanism:

$$Cr(III)_{aq} + P \rightleftharpoons Cr(III) \cdots P \xrightarrow{k_1} Cr(III)-(P) \qquad (S1)$$

$$Cr(III)-(P) + P \xrightarrow{k_2} Cr(III)-(P)_2$$

where Cr(III)⋯P is in a rapid equilibrium/steady state with uncomplexed Cr(III) and polymer P, and is slowly forming HPAM−coordinated Cr(III) species.

A parallel mechanism including formation of an outer-sphere complex prior to Cr(III)−HPAM cross-link formation is also possible:

$$Cr(III)_{aq} + P \rightleftharpoons Cr(III) \cdots P \xrightarrow{k_1} Cr(III)-(P)$$

$$Cr(III)-(P) + P \xrightarrow{\text{fast}} Cr(III)-(P)_2 \qquad (S2)$$

$$Cr(III)_{aq} + P \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\text{byproduct})$$

The rate equation of mechanism M1−M7 in the excess of polymer carboxylate groups is given by

$$v = k_1[Cr(H_2O)_6^{3+} \cdots PCOO^-] + k_{1'}[Cr(H_2O)_5OH^{2+} \cdots PCOO^-] \qquad (8)$$

Applying the equilibrium equations of reactions M1−M5 and the mass balances of Cr(III) and polyacrylamide, the rate equation becomes

$$v = \frac{(k_1 K_{M4}[H^+] + k_{1'} K_{M5} K_{M2}) K_{m1}[P]_0 [Cr(III)]_{unr}}{([H^+] + K_{M1})([H^+] + K_{M2}) + (K_{M4}[H^+] + K_{M5} K_{M2}) K_{M1}[P]_0} \qquad (9)$$

where v is the rate, K_i is an equilibrium constant of process i, $[Cr(III)]_{unr}$ is the sum of unreacted Cr(III) species including the outer-sphere complexes, and $[P]_0$ is the total polymer carboxylate concentration. The deduction of eq 9 is based on the assumption that the concentrations of outer-sphere complexes and reacted polymer are small relative to the total polymer concentration. Also the second hydrolyzed Cr(III) ion formed by reaction M3 is neglected. The derivation of eq 9 is shown in more detail in the supplementary material.

Conclusion

The initial phase of the Cr(III)−HPAM cross-linking reaction follows saturation kinetics in HPAM and is first order with respect to Cr(III). Experiments and simulations of different mechanisms indicate that the reaction observed initially is the binding of the first HPAM chain to Cr(III). But both purely consecutive mechanisms as well as mechanisms with additional parallel reactions are possible to account for the observed biphasic behavior in the pseudo-first-order plots.

Supplementary Material Available: Rate equations of two reversible consecutive or parallel reactions, requirements of rate constants and molar absorptivities to simulate the spectroscopic behavior of a biphasic reaction with consecutive or parallel reactions, and deduction of the rate equation (eq 4) (8 pages). Ordering information is given on any current masthead page.

References and Notes

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