Synthesis, Evaluation, and Gelation Mechanism of Organic Chromium

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ABSTRACT: Since the launching of tertiary oil recovery, the performance requirements of polymer solution increasing, the polymer solution is more difficult to meet the needs of the scene. It could solve poor profile control, salt-tolerant, and poor performance that crosslinking agent was added to polymer solution. Therefore, chromium acetate crosslinker was synthesized, and the synthesis conditions were optimized, and the performance of crosslinking agent was evaluated. Through optimization, the optimum conditions of chromium acetate synthesis was: reaction time 10 h, reaction temperature 80°C, the molar ratio of acetic acid and potassium dichromate than or equal to 24 : 1. Performance evaluation showed that adding crosslinking agent could significantly increase the viscosity of the polymer solution, could significantly improve the resistance coefficient and residual resistance of the polymer solution, and could play a good role profile flooding. Studies showed that when salinity and ion content changed, the crosslinking mechanism of changed. Through the study of molecule coil size at room temperature, the molecule coil size would slightly decline after 1 h, suggesting that crosslinking mechanism was intramolecular crosslinking reaction occurs at first, and then intermolecular crosslinking reaction. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3669–3677, 2012

Key words: acetate chromium; crosslinking agent; mineralization; intramolecular crosslinked; intermolecular crosslinked

INTRODUCTIONS

In the process of water flooding, the heterogeneity of the formation and injected water erosion caused by long-term damage to the rock structure, causing part of the reservoir 80–90% of injected water was absorbed by the high permeability.[1] Low permeability layer to increase the amount of fluid absorption and improve the sweep efficiency of injected water, the water injection wells must be adjusted profile. To partially hydrolyzed polyacrylamide (HPAM) as a flooding agent for polymer flooding technology in the domestic oil gained wide application and success,[2–4] but the polymer flooding technology still has some problems: HPAM has poor salt resistance performance, the viscosity of HPAM solution prepared by sewage water reduced obviously than prepared by clean water, HPAM has poor heat resistance, HPAM can be applied to the maximum temperature 75°C,[5–7] HPAM is easily interporosity flow in the oil reservoir, the ability of adjusting the profile is weak, oil field need large amount of HPAM, so it is difficult to further reduce costs. To improve the application of polymer flooding effect, extend the scope of application of polymer flooding, it is necessary to improved polymer performance. It is simple and effective way to add crosslinking agent to the polymer. Chromium crosslinking agent is the most promising one,[8] it can be in a wide range of temperatures and pH values within the control of gelation, crosslinker is a highly adaptable. In this article, the synthesis conditions of chromium acetate crosslinker were optimized, various factors of synthesis conditions on the gelling properties were compared, and crosslinker was evaluated, the change of the molecular coil size was studied in the crosslinking process, and the mechanism was speculated, it is very important to deeply study the crosslinking process of HPAM/Cr^{3+} gel and the change of polymer molecular configuration, and it is very important for the mine to improve the effect of increasing oil polymer flooding technology, to promote HPAM/Cr^{3+} gel flooding.

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EXPERIMENTAL

Chemicals and equipment

Potassium dichromate (AR, effective content 99.8%), acetic acid (AR, effective content 36%), sodium nitrite (AR, effective content 99.5%), barium chloride (AR, effective content 98%), ammonia (AR, effective content 25%), Standard buffer solution pH value, potassium dihydrogen phosphate (AR, effective content

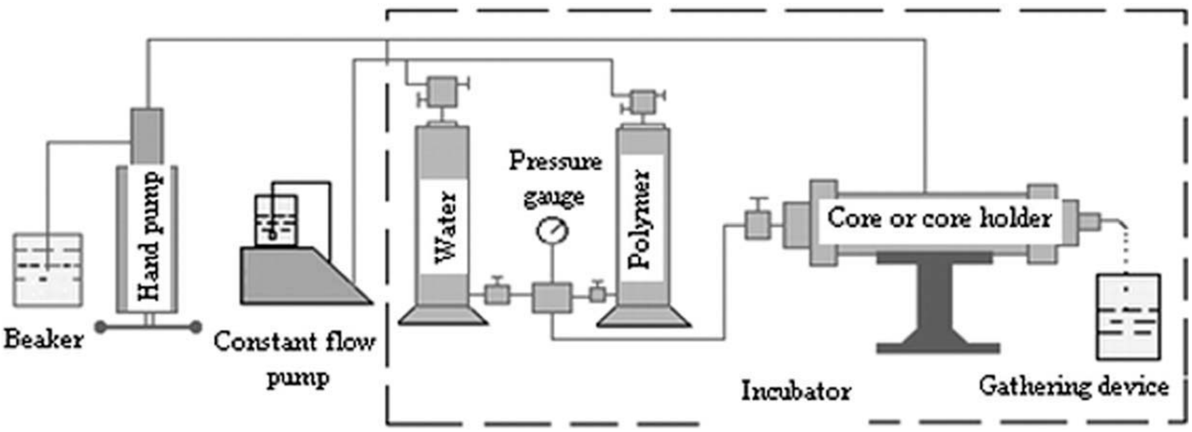

Figure 1 Experiment instruments and flow chart.

98%), KCl (AR, effective content 99.8%), and Daqing Refining and Chemical Company production partially hydrolyzed polyacrylamide polymer (HPAM; relative molecular weight of 1900×10^4, active ingredient of 88.0%, and degree of hydrolysis of 24.2%), and so on.

Model PHS-3C digital pH meter(Shanghai ray magnetic instrument plant, China), KDM Electric Adjustable temperature control sets (JuanCheng hua lu electric instrument, China), KJ-1 laboratory stirrer (Shanghai than lang instrument, China), glass condenser (Tianjin glass instrument plant, China), three-neck flask (Tianjin glass instrument plant, China), and so on.

Viscosity of each sample was measured systemically by an Brookfield DV II+pro Programmable Viscometer (made by Brookfield Engineering Laboratories), the rotational speed was 6 rev/min, the measurement range of 0 # rotor was 0–99, the measurement range of 1 # rotor was 100–999.9, the measurement range of 2 # rotor was 1000–4999, the measurement range of 3 # rotor was 5000–19,999, the measurement range of 4 # rotor was 20,000–99,999.

The molecule coil size testing apparatuses were BI-200SM Model Wide-angle Dynamic/Static Light Scattering Instrument System (made by Brookhaven Instruments).The main components included a BI-9000AT Laser Correlator, a Signal Conditioner and an Argon Ion Laser (200 mW, laser wavelength is 532.0 nm) at a scatter angle of 90°. Before measurement, containers such as bottles were cleaned thoroughly by a KQ3200DE NC Ultrasonic cleaner.

Flow property of the polymer or crosslinked polymer solution involves injection pressure, resistance coefficient and residual resistance coefficient. As technical indices, resistance coefficient, F_R, and residual resistance coefficient, F_{RR}, are used to describing the remnant amount of polymer or crosslinked polymer solution within porous media, which can be calculated by the equations as follows:

$$F_R = \delta P_1/\delta P_0, F_{RR} = \delta P_2/\delta P_0$$

where δP_0 is the stable pressure difference between the two ends of the core when the water is injected in the core, δP_1 is the stable pressure difference when the slug of polymer solution is injected, and δP_2 is the stable pressure difference when the driving fresh water is injected. In the test, injected rate should be at a constant flow rate and the injected pore volume should be 3 PV at least, then succeeding water was injected to stable pressure.

The experimental apparatuses of flow property test include advection pump, pressure sensor, core holder, hand pumps, and intermediate containers. In addition to advection pump and hand pump, the other part of them to a certain temperature, the thermostat box. Laboratory equipment and process are shown in Figure 1. Mobility before the experiment, the shear of polymer solution, viscosity retention rate was 60%.

Reaction mechanism

Cr^{6+} ions of sodium nitrite will be reduced to Cr^{3+} ions, organic acids and Cr^{3+} complex, the formation of organic acid chrome complexes.

Main reaction: $Cr_2O_7^{2-} + 3NO_2^- + 8H^+ = 2Cr^{3+} + 3NO_3^- + 4H_2O$

Side effects: $Cr_2O_7^{2-} + 6NO_2^- + 14H^+ = 2Cr^{3+} + 6NO_2\uparrow + 7H_2O$

Acetic acid: $K_2Cr_2O_7$ = 22–48 : 1 (molar ratio); $NaNO_2 : K_2Cr_2O_7$ = 3.1–3.5 : 1 (molar ratio).

Experimental procedure

Procedure of crosslinker synthesis

(1) A certain amount of acetic acid was added into the three-neck flask, then a certain amount of potassium dichromate was put into, when they was fully dissolved in the case of stirring, and sodium nitrite

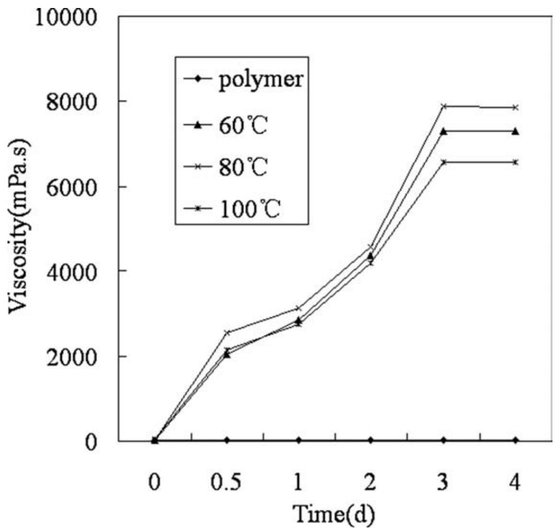

Figure 2 Relation between reaction time and the viscosity of the gel. (The horizontal axis represents crosslinking time under the same temperature.)

was added slowly. (2) Then the electric heating was set to 60–100°C, after a certain time, then the three-neck flask was cooled down to room temperature. (3) $BaCl_2$ solution and distilled water were used to detect the reaction of Cr^{6+} is complete or not, if the reaction is complete, then the next step was carried, if not an appropriate amount of sodium nitrite should be added, turned to (2). (4) Finally, the pH of solution was adjusted with ammonia.

Procedure of crosslinker properties evaluation

(1) Put a certain amount of HPAM into the water in the case of stirring, churn ceaselessly 2–4 hours, make its dissolve completely. (2) Put a certain amount of crosslinker into the polymer solution in the case of stirring, churn ceaselessly 20 minutes. (3) Test the viscosity, molecule coil size or flow property of HPAM/Cr^{3+} gel. (4) Put the HPAM/Cr^{3+} gel into the incubator if test the influence of time.

RESULTS

Reaction conditions on the performance of crosslinking agent

The reaction conditions (such as reaction time, reaction temperature, and reactant ratio) have a great influence on performance of gelling properties of crosslinker. Gelling properties of crosslinker was evaluated. According to the evaluation results, we can get the optimal synthesis conditions.

Experiments was prepared: polymer solution concentration was 1000 mg/L, the ratio of polymer to Cr^{3+} was 60 : 1, the test temperature was 33°C, the water was Fuyu sewage.

Influence of synthesis reaction time

The results that different synthesis reaction time of crosslinker has influence on the gelling properties of crosslinker are shown in Figure 2.

As shown in Figure 2, crosslinking reaction time has influence on gelling properties of crosslinker. The same concentration of crosslinking agent, when synthesis reaction time was 10–20 h, the gelling properties of crosslinker was better, and the increasing range of gel viscosity was bigger. Therefore, optimum synthesis reaction time was 10 h. When reaction time is too short, the reaction is not sufficient; when reaction time is too long, the increment of gel viscosity is not obvious.

Influence of synthesis temperature

The results that different synthesis temperatures have influence on the gelling properties of crosslinker are shown in Figure 3.

Figure 3 shows that the synthesis temperature has effect on gelation properties of crosslinker. Under the same ratio of polymer to Cr^{3+}, synthesis temperature is 80°C, gelling properties of synthesis crosslinker is best, and the increasing range of gel viscosity was biggest. When the temperature is too low, the reaction is not sufficient; when the temperature is too high, side effects may occur, resulting in lower viscosity of HPAM/Cr^{3+} gel.

Influence of reactant ratio

The results that different ratio reactants have influence on gelling performance of crosslinker are shown in Figure 4.

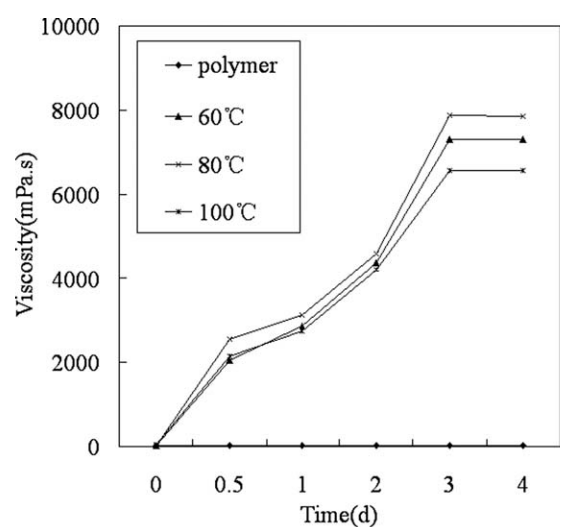

Figure 3 Relation between reaction temperature and the viscosity of the gel and the polymer. (The horizontal axis represents crosslinking time under the same temperature.)

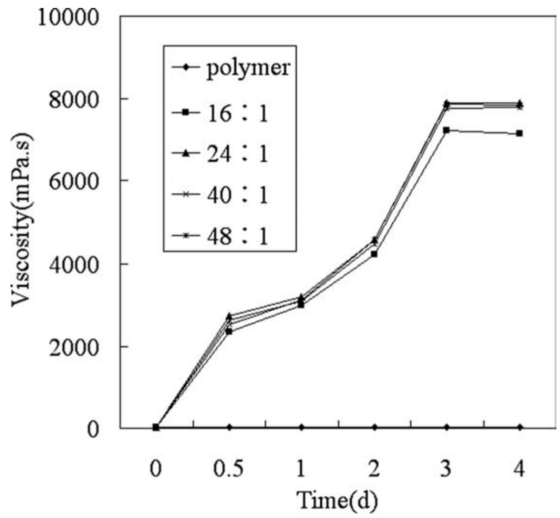

Figure 4 Relation between the ratio of reactants and the viscosity of the gel and the polymer. (The horizontal axis represents crosslinking time under the same temperature.)

Figure 4 shows the proportion of acetic acid and potassium dichromate has effect on gelation properties of crosslinker. When the molar ratio of acetic acid and potassium dichromate is 16 : 1, gelling properties of synthesis crosslinker is worse, when the molar ratio of acetic acid and potassium dichromate is 24 : 1 to 48 : 1, gelling properties of synthesis crosslinker is better. This shows that the least molar ratio of acetic acid and potassium dichromate is 24 : 1.

Influence of pH value

The results that pH value of crosslinker has influence on the gelling properties of crosslinker are shown in Table I.

Table I shows that all crosslinkers (pH = 4.6, 7.0, or 8.5) can make the viscosity of the gel increase, indicating that the crosslinking reaction occurred. And the pH value of the crosslinker increases, the viscosity of the gel increases. The reason is that, after the addition of Cr^{3+} crosslinker, three reactions occurred in polymer solution[9]:

$$\mathrm{mCr^{3+} + xH_2O \overset{Hydrolysis}{\rightleftharpoons} Cr^{3+} - Polynuclear\ complex\ ion\ hydroxyl\ bridge + nH^+} \quad (1)$$

Before the crosslinking reaction of polymer solution occurred, the ionization of polymer must take place.

$$\mathrm{R - COOH \overset{Ionization\ equilibrium}{\rightleftharpoons} R - COO^- + H^+} \quad (2)$$

TABLE I
Performance Evaluation of Different pH, the Results of Crosslinking Agent (mPa.s)

	Time (day)					
Crosslinker	0	0.5	1	2	3	4
pH = 4.6	29.7	157	293	359	819	961
pH = 7.0	30.5	458	887	1614	3721	3735
pH = 8.5	30.1	2540	3120	4587	7890	7854

Note: Cp = 1000 mg/L, the ratio of polymer to Cr3+ was 60 : 1, test temperature was 33°C.

$$\mathrm{R - COO^- + Cr^{3+} - Multinuclear\ olation\ complex\ ions \xrightarrow{rosslinking} Crosslinked\ polyme} \quad (3)$$

As the H^+ takes part in the process, so the pH value of the system has significant impact on the gelling process. In the crosslinking process, the step (2) that the $RCOO^-$ generates is a weak acid ionization process, fast response, easy to achieve balance, it is not a the speed control step, so the control step(s) is the step (1) or(and) step (3). Polymer gelling process is a diffusion reaction process that interdiffusion of polymer and Cr^{3+} multinuclear olation complex ions is the control step, so the step (3) is the control reaction. In suitable pH value range, with the increase of pH value, H^+ concentration decreases, the step (1) will shift to the right, the Cr^{3+}multinuclear olation complex ions concentration will increase, the average spacing between the Cr^{3+}hydroxide polymers decreases, the limited space that Cr^{3+}hydroxide polymer moves, spreads and distributes also decreases, the limited spacing of polymer chain growth decreases, the arrangement of closely linked, the size of network gel becomes small and dense, density increases, the intensity of gel increases. At the same time the step (3) is the rate limiting step, with the pH value increases, the concentration of Cr^{3+} multinuclear olation complex ions will increase, the diffusion rate of the gel accelerates, reaction time is reduced.[10] However, the pH value

TABLE II
The Concentration of Polymer Gels and the Relationship Between Viscosity (mPa.s)

Time (day)	Polymer concentration (mg/L)				
	800	1200	1600	2000	2400
0	16.3	45.2	72.2	291.9	451
1	69	1600	2095	2560	4099
3	91	2051	7910	14,800	18,600
5	89	2045	7854	13,852	18,450

Note: The ratio of polymer to Cr^{3+} was 60 : 1, test temperature was 33°C.

TABLE III
Relation Between the Ratio of Polymer to Cr^{3+} and the Viscosity of the Gel and the Polymer (mPa.s)

Time (h-hour; d-day)	Polymer : Cr^{3+}					
	0	30 : 1	60 : 1	120 : 1	180 : 1	360 : 1
0[a]	38.1	35.6	36.6	37.1	37.5	37.7
1 h[a]	38.3	35.2	36.2	36.8	37.3	37.2
1 d[a]	38.5	49.2	48.5	48.8	47.9	38.9
0 d	30.1	29.1	28.5	29.4	29.3	29.5
1 d	32.1	12457	2085	421	174	30.6
3 d	40.2	27541	7890	1251	430	32.5

Note: Cp = 1000 mg/L, test temperature was 33°C.
[a] Represented that the samples were stood and tested at 25°C.

of crosslinker cannot be too high; otherwise, it will lead to production of Cr^{3+} precipitation.

Compare each factors, the pH value was very important, second was the synthesis reaction time, and synthesis temperature. Finally is reactants proportion. So It's very necessary to adjust pH value of the crosslinker solution to 8–9 using ammonia.

Gelling properties evaluation of gel crosslinker

Influence of polymer solution concentration on the gelling properties

The results that polymer solution concentration has influence on the gelling properties of crosslinker are shown in Table II.

As shown in Table II, the concentration of polymer solution has a certain influence on the crosslinking properties of the crosslinker. With the increase in polymer concentration, the viscosity of HPAM/Cr^{3+} gel increases. Therefore, the crosslinker has good performance of crosslinking.

Table II also shows that, the time has a certain influence on the crosslinking properties of the crosslinker. With the increasing of time, the viscosity of the HPAM/Cr^{3+} gel increased gradually at first, and then basically unchanged. That at a certain temperature, in order to make the gelling Cr^{3+} system will take some time. It will take some time that make the polymer solution into a gel.

Influence that the ratio of polymer to Cr^{3+} on the gelling properties of crosslinker

The results that the ratio of polymer to Cr^{3+} had influence on the gelling properties of crosslinker are shown in Table III.

As shown in Table III, the ratio of polymer to Cr^{3+} has a certain influence on the gelling properties of crosslinker. With the decrease in the ratio of polymer to Cr^{3+}, the viscosity of the HPAM/Cr^{3+} gel gradually increases. This reason is that the bigger is concentration of crosslinker, the greater is probability of contact with the polymer and crosslinker, more easily molecule chains grafts with each other, and intermolecular crosslinked network structure form, the viscosity of the gel increases significantly. The research[11] also shows that, the gelation time of the HPAM/Cr^{3+} gel will be shortened with the increase in crosslinker concentration, the viscosity of the formation gel increased with the increase in crosslinker concentration. The studies[12] suggest that the ratio of polymer to Cr^{3+} is an important factor to control the performance of the polymer gel. With the molar ratio of Cr^{3+} to polymer increased, the

TABLE IV
Relation Between the Ratio of Polymer to Cr^{3+} and the Molecular Coil Size of the Gel and the Polymer (nm)

Time (h-hour; d-day)	Polymer : Cr^{3+}					
	0	30 : 1	60 : 1	120 : 1	180 : 1	360 : 1
0 h[a]	101.2	96.3	99.7	100.8	100.5	100.8
1 h[a]	102.5	94.3	94.7	98.6	98.9	99.0
1 d[a]	106.2	100.9	102.5	102.3	103.6	101.9
0 d	110.5	99.8	102.5	102.9	103.6	108.9
1 d	119.2	458.3	421.5	385.2	344.1	198.7
3 d	119.5	875.6	653.1	458.2	430.2	235.4

Note: Cp = 100 mg/L, test temperature was 33°C.
[a] Represented that the samples were stood and tested at 25°C.

TABLE V
The Influence Results That Temperature on the Properties of Crosslinker (mPa.s)

Oil displacement agent	Test temperature (°C)				
	35	45	55	65	75
Polymer solution	23.1	23.8	23.4	24.3	23.7
Polymer gel	30.1	30.5	37.1	4542	6892

Note: Cp = 1000 mg/L, the ratio of polymer to Cr^{3+} was 60 : 1.

strength of gel increased, the sealing capacity enhanced.

The results that the ratio of polymer to Cr^{3+} has influence on the molecular coil size are shown in Table IV.

As shown in Table IV, standing time and the ratio of polymer to Cr^{3+} have a certain influence on the molecular coil size. At the 33°C and the same of polymer to Cr^{3+}, with the increasing in time, the molecular coil size gradually increases. At the 33°C and the same standing time, with the decreasing in the ratio of polymer to Cr^{3+}, the molecular coil size gradually increases. When the samples were stood and tested at the 25°C, the molecular coil size of the gel slightly decreases at 1 hour, then increases.

Influence of temperature on the gelling properties of crosslinker

The results that temperature has influence on the gelling properties of crosslinker are shown in Table V. As shown in Table V, the test temperature has influence on the *t* into the gelling properties of crosslinker. With the temperature increasing, the viscosity of the polymer gels changed little at first, and then increased rapidly. The reason is that, the higher the temperature, the faster the thermal motion of molecules, the faster spread of the polymer molecules, and the higher the chance of crosslinker exposures, leading to faster gelation. The researches[8] suggest that Cr (III) system would gel more quick, even could not control at 60°C or higher temperature. The Cr^{3+}/HPAM micro-gel system studies[13] also found that, the temperature of the Cr^{3+}/HPAM system had a great influence on gel properties, the higher the temperature the faster the crosslinking reaction, the shorter the gelation time.

Influence of water on the gelling properties of crosslinker

The results that water had influence on the gelling properties of crosslinker are shown in Table VI. As shown in Table VI, water has influence on gelling properties of the crosslinker. The viscosity of HPAM/Cr^{3+} gel prepared Fuyu water was significantly higher than the viscosity of polymer solution, and the viscosity significantly increased with the time increased; but the viscosity of HPAM/Cr^{3+} gel prepared LD10-1(a well of China National Offshore Oil Corporation) water approached the viscosity of the polymer solution, and there was not significant change with the increasing of time. It showed that crosslinking reaction took place among different polymer molecules chains prepared Fuyu water, namely the intermolecule crosslinking reaction. Unlike molecular structure of polymer, this kind of HPAM/Cr^{3+} gel showed a "regional" network-like molecular structure,[14] leading to a substantial increase in the viscosity of the polymer gel. However, the viscosity of HPAM/Cr^{3+} gel prepared LD10-1 water increased slightly. It also showed that crosslinking reaction mainly took place in different chains of the same polymer molecule or did not take place. The crosslinking reaction is known as the intramolecule crosslinking reaction, and this kind of HPAM/Cr^{3+} gel showed a different molecular structure. That is, a "local" network-like molecular structure.[14] The main reason was the preparation of polymer gels with different water salinity (salinity and ionic composition in Table VII). The salinity, Ca^{2+} and Mg^{2+} ion content is higher, the polymer molecules tend to curl more and more prone to intramolecular crosslinked, on the contrary, prone to intermolecular crosslinked.[14]

Flow characteristics of chromium ion HPAM/Cr^{3+} gel experiments

The flow performance test results are shown in Table VIII. As shown in Table VIII, the ratio of

TABLE VI
The Influence Results of Water (mPa.s)

Displacing agent		Time (d)					
		0	0.5	1	2	3	4
Sewage water of Fuyu	Polymer solution	23.4	24	24.2	24.8	25	24.6
	Polymer gel	30.1	2540	3120	4587	7890	7854
Clean water of LD10-1	Polymer solution	4.4	4.4	5.2	4.6	4.4	4.4
	Polymer gel	4.5	5.6	5.8	5.7	5.5	5.6

Note: Cp = 1000 mg/L, the ratio of polymer to Cr^{3+} was 60 : 1, test temperature was 33°C.

TABLE VII
Ion Content Analysis

	Ion composition and content (mg/L)							Total salinity (mg/L)
	$K^+ + Na^+$	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	
Clean water of LD10-1	2968.84	826.65	60.8	6051.6	60.04	0	208.69	10176.62
Sewage water of Fuyu	1002.80	68.14	13.37	682.41	4.80	75.01	1601.78	3448.31

polymer to Cr^{3+} has influence on the resistance coefficient and residual resistance coefficient of HPAM/Cr^{3+} gel prepared LD10-1 water. With the same polymer concentration and gas permeability, the ratio of polymer to Cr^{3+} was bigger, Cr^{3+} concentration was lower, the resistance coefficient and residual resistance coefficient was smaller. Further analysis found that, the drag coefficient and residual resistance coefficient of HPAM/Cr^{3+} gel is much larger than the polymer solution. This further explained that crosslinking reaction mainly took place in different chains of the same polymer molecule in HPAM/Cr^{3+} gel prepared the LD10-1 water, that is, "intramolecular" crosslinked.

It is found that crosslinking reaction of polymer solution prepared by different water is different, crosslinking reaction mainly takes place in different chains of the same polymer molecule chain prepared LD10-1 water, that is, "intramolecular" crosslinked; but crosslinking reaction take place among different polymer molecules chains prepared Fuyu water, that is, "intermolecular" crosslinked. Different salinity of the water is the main reason that the structure of HPAM/Cr^{3+} gel molecular is different, because the mineralization is the main effect factor of degree of the polymer molecular chains extension. According to Stern-Grahame double-layer theory,[15] the higher the salinity, the concentration of Na^+, K^+, Ca^{2+}, and Mg^{2+} higher, when the polymer dissolved in high salinity water, the Na^+ and K^+ charge that is opposite with the surface charge of polymer chains will transport to the Stern layer, some will enter the Stern layer, neutralize partial charge of the molecular surface, this will reduce the diffusion layer thickness, ζ electric potential drop, then will lead to polymer chains curl and shrink (Fig. 5), and exclude encapsulated water molecules, make the probability smaller that different polymer chains contact with each other, and crosslinker will play a role in the small range, so that the different branched chains of same polymer molecule will contact with each other form a "partial" crosslinked network structure,[14] that is, "intramolecular" crosslinked. Therefore, the crosslinker will make the branched-chains of the same polymer molecule crosslink each other in the high salinity water, form localized network structure.[14,16,17] On the contrary, the crosslinker will make the branched-chains of different polymer molecules crosslink, form space network structure.

The electrolyte type and concentration had influence on crosslinking reaction of AlCit in HPAM,[18] the results show that high electrolyte concentration is conducive to intramolecular crosslinking reaction, in which the effect of Ca^{2+} is better than Mg^{2+}, Mg^{2+}, better than Na^+. Therefore, the intermolecular crosslinked took place in the polymer solution prepared by Fuyu sewage, while the intramolecular crosslinked took place in the polymer solution prepared by LD10-1.

CROSSLINKING REACTION MECHANISM

By analysing the changing process of the HPAM/Cr^{3+} gel viscosity and molecular coil size, the crosslinking mechanism could be predicted. According to the theory of fractal growth[19] and Stern-Grahame double-layer theory,[15] the difference of electrolyte, crosslinker and polymer concentration is the main reason, which made the molecular structure of the HPAM/Cr^{3+} gel vary. In the polymer solution, the molecule chains of partially hydrolyzed polyacrylamide (PHPA) have carboxyl anions, the adjacent carboxyl anions repel each other, so the molecule chains of PHPA extends.

TABLE VIII
The Experimental Data of Resistance Coefficient and Residual Resistance Coefficient

	The ratio of polymer to Cr^{3+}							
	0		270 : 1		360 : 1		540 : 1	
Displacing agent	F_R	F_{RR}	F_R	F_{RR}	F_R	F_{RR}	F_R	F_{RR}
Cr^{3+} Polymer gel (Clean water of LD10-1)	8.5	3.2	1967	Block	548.4	1709.7	483.9	1306.5

Note: CP = 1000 mg/L, the gas permeability is about 2400×10^{-3} μm^2.

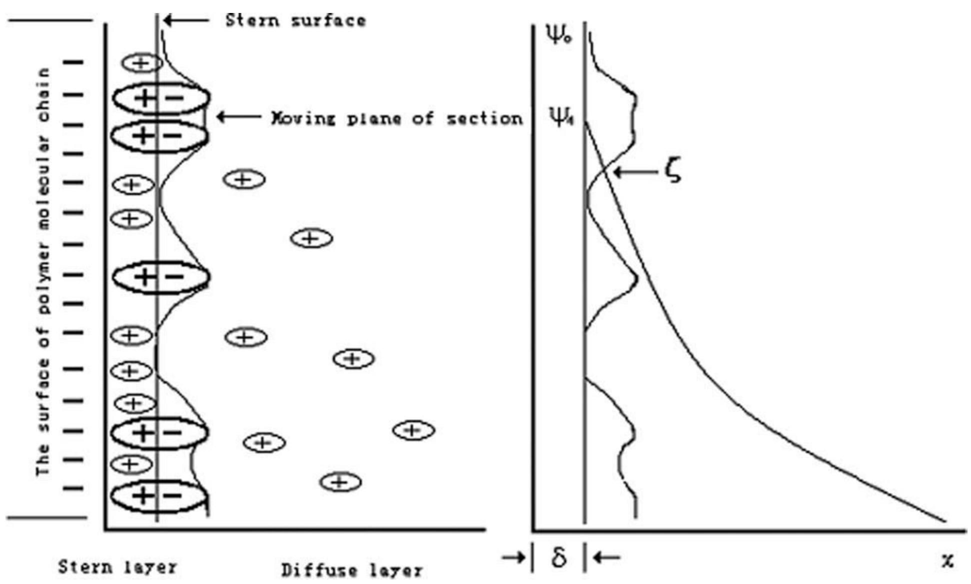

Figure 5 Stern-gel molecular surface diagram of double-layer model.

When the cation concentration is higher in water, these cations would move to the surface Stern layer, part of the cations would enter into the Stern layer to neutralize the negative charge of the PHPA molecular chain surface, that would make the thickness of the polymer molecular diffusion layer reduce, molecular chains curl, and coil size decrease. And the contact between chains of different molecules would be difficult than different chains of the same molecule. (1) At this point, crosslinker is added to the polymer solution, the intramolecular crosslinking reaction of the different branched-chains in the same polymer chains takes place, molecular configuration shrinks, and forms compact clew, that can be called single molecule clew, like a ball, in the process the viscosity of polymer solution has little change, but the molecular coil size slightly decreases, this is induction period. (2) Then the crosslinking reaction would take place between the balls, this is to say intermolecular crosslinked. The intermolecular crosslinking reaction takes place continuously in the process, crosslinking points increases continuously in unit time, thus the molecular coil size increases gradually, the viscosity of polymer solution increases rapidly, results in accelerated period. (3) When the intermolecular crosslinking reaction finished, the viscosity of polymer solution does not change, is the stable phase. Therefore, the intramolecular crosslinked forming single-molecule ball takes place in the induction period, intermolecular crosslinking reaction, which would gradually form network structure mainly takes place in accelerated phase.

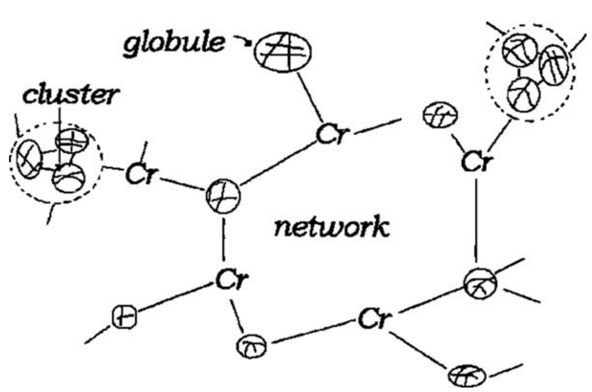

Figure 6 The molecular structure of the crosslinking reaction of polymer morphology diagram. "Globule" represents the intra-molecule cross-linked, and "cluster" and "network" represent the inter-molecule cross-linked.

All the reactions (1), (2), and (3) took place in the HPAM/Cr^{3+} gel prepared Fuyu water(Tables III and IV; polymer : Cr^{3+} = 30 : 1–180 : 1), but the reaction (1) took place in the HPAM/Cr^{3+} gel prepared LD10-1 water, because the salinity is higher, the cation concentration is higher, which made the molecular chains more curly, so that the chains of different molecules had very little contact between each other, so the reactions (2) and (3) hardly took place. When the salinity is lower, the concentration of crosslinker and polymer was lower the reactions (2) and (3) hardly took place (Tables III and IV; Fig. 6; polymer : Cr^{3+} = 360 : 1).

CONCLUSIONS

1. The experimental results show that the optimal synthesis conditions of chromium acetate crosslinker are: reaction time is 10 h, reaction temperature is 80°C, the molar ratio of acetic

acid, and potassium dichromate is greater than 24 : 1.

2. Must adjust pH value of synthetical crosslinker to a reasonable range, too high will form deposit, too low will result in the gelling properties of crosslinker worse.
3. Polymer concentration, the ratio of polymer and Cr^{3+}, temperature, and water has influence on gelling properties of polymer gels.
4. Water-different (i.e., different water salinity and different concentration of calcium and magnesium) could make HPAM/Cr^{3+} gel take place intermolecular crosslinked or intramolecular crosslinked. Intermolecular crosslinked will make the viscosity increase, and intramolecular crosslinked does not make the viscosity of HPAM/Cr^{3+} gel increase significantly, but intramolecular crosslinked will make resistance coefficient and residual resistance coefficient increase significantly.
5. The intramolecular crosslinked reaction first takes place, then the intermolecular crosslinking reaction occurs, this is the crosslinking mechanism of the Cr^{3+} polymer gel.

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