

# Characterization of the Formation and Degradation of a Polyacrylamide Microgel

Fangeng Chen,<sup>1</sup> Hongjuan Wang,<sup>1</sup> Chuanfeng Zhu,<sup>2</sup> Lingling Ren,<sup>2</sup> and Jing Li<sup>3</sup>

<sup>1</sup>Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China

<sup>2</sup>Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>3</sup>Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China

Received 27 January 2004; accepted 19 May 2004

DOI 10.1002/app.20967

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The morphology of polyacrylamide microgel in gelation and degelation procedures is characterized by atomic force microscopy. The polymer concentration, the cross-linker concentration, and the type of cross-linker have significant influence on the microstructure of polyacrylamide. The changes in aggregation status result in changes

in the rheological properties of the polymer solution and microgel. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1375–1380, 2004

**Key words:** microgels; microstructure; atomic force microscope; gelation

## INTRODUCTION

Gelling fluids are widely used today to improve petroleum production. During a well treatment process, the fluids are injected into the fractures or highly conductive zones to form elastic gels. The permeability of problem zones is thus reduced and the injected water can be diverted to the unswept zones. More petroleum can thus be produced.

Microgel, which was proposed in the 1960s,<sup>1</sup> is different from normal polymer gels and is a colloid-like, flowable, and irregular gel. It is an intramolecularly cross-linked macromolecule, that is dispersed in normal or colloidal solutions, depending on the degree of cross-linking and on the nature of the solvent.<sup>2</sup>

The viscosity of the microgel is higher than that of the polymer solution of same concentration, but it is much lower than that of the normal polymer gel. This property makes it suitable for reducing the flow of water substantially through the regions contacted by the gel. Microgel can also act as a sweeping fluid. Microgel has a higher viscosity the polymer solution of the same concentration than that of addition of a small amount of polymer can achieve moderate gel viscosity. Such properties make it possible to significantly decrease the cost of the gelling fluids.

Organic salts, especially chromium carboxylate, are widely used as the cross-linker in preparing

microgels.<sup>3–5</sup> Low-cross-linked phenolic aldehyde resins are sometimes used in order to prolong the gelation.

The variations of the rheological properties of polyacrylamide during the gelation procedure and the structure of the microgel have been investigated in detail.<sup>4</sup> Chen et al.<sup>3</sup> studied the microstructure of polyacrylamide microgel and found that microgel eventually formed self-assembly branch-like fractal structures. Zhang et al.<sup>6</sup> investigated the gelation behavior and the morphological structure of HPAM/lead citrate microgel by optical microscopy. However, the changes in the microstructure of polyacrylamide during the gelation and degelation procedure have seldom been studied.

In this paper, the changes in microstructure of the polyacrylamide during the gelation and degelation procedure are characterized by atomic force microscopy (AFM). The differences in the gelation behavior of the gelling fluids cross-linked with different cross-linkers are compared. The relationship between the microstructure and the viscosity of the gelling fluids is also investigated.

## EXPERIMENTAL

### Materials

Polyacrylamide, 3530S (molecular weight  $1.7 \times 10^7$ , 21.0% hydrolyzed), was the commercial product of SNF Flocculant Co., Ltd. (France). Other reagents were of CP or AR grade.

Correspondence to: F. Chen (fgchen@gdgc.cnuninet.net)

**TABLE I**  
**Sample Compositions and Pretreatment Methods**

Sample no.	Polymer concentration (mg/L)	Cross-linker	Cross-linker concentration (mg/L)	Aging time (h)
1	80	None	0	0
2	600	None	0	0
3	600	Chromium acetate	100	0
4	600	Chromium acetate	100	5
5	600	Chromium acetate	100	12
6	600	Chromium acetate	300	12
7	600	Chromium acetate	100	360
8	600	Phenolic aldehyde	600	240
9	600	Phenolic aldehyde	1000	240
10 <sup>a</sup>	1000	None	0	0
11 <sup>a</sup>	1000	Chromium acetate	100	24

<sup>a</sup> The polymer solutions were stirred at a rate of 10,000 r/min for 30 s.

## Methods

Two kinds of cross-linkers, i.e., chromium acetate and phenolic aldehyde resin, were used in this experiment. Chromium acetate was prepared by reacting chromium chloride with sodium dichromate and acetic acid. Phenolic aldehyde was prepared by reacting phenol with formaldehyde in the presence of sodium hydroxide.

A stock solution of polyacrylamide and a stock solution of cross-linkers and other chemicals, as well additional water were added into the vial according to the compositions listed in Table I. The pH was adjusted to 6.5. Then the solutions except for Samples 1, 2, 3, and 10 were aged at 80°C in a forced-air oven. Finally, all samples were transferred onto a newly cleaved mica sheet, spread, and warmed to form a film.

The microcosmic shape of the gel was observed using a NanoScope III SPM/AFM manufactured by Veeco Corp. at room temperature using the tapping mode. Topographic images were recorded using the retrace signal. Si cantilever tips with a resonance frequency of  $\sim 300$  Hz and a spring constant of  $\sim 40$  Nm<sup>-1</sup> were used. The scan rate was in the range of 0.5 to 1.5 Hz/s. The sample line was 512 and the target amplitude was 2 V.

The viscosities of the gel-forming fluids and the microgels were measured using a Brookfield rotary viscometer at 30°C.

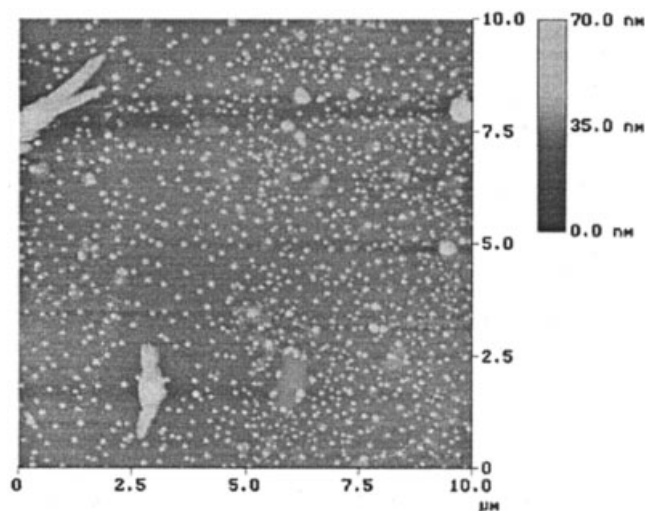
## RESULTS AND DISCUSSION

The variations in microstructure of polyacrylamide before gelation, after gelation, and after degelation were recorded. The influences of polymer concentration, cross-linker concentration, and temperature on the microstructures of polymer were studied. The images were compared with the viscosity data of the gelling fluids and microgels.

### Microstructure of polyacrylamide in gelling fluids

Figure 1 shows the topographical image of the polymer film formed from an 80 mg/L polyacrylamide solution. Many tiny particles are distributed in the whole scanning range. The average diameter of the particles is 56.1 nm. These particles represent the agglomerated polyacrylamide molecules. The microstructure doesn't change despite the addition of 100 mg/L of chromium acetate.

The film from a 600 mg/L polyacrylamide solution presents fractal branches, as shown in Figure 2. It has been reported in the literature that the branches were accumulated by tiny spherical particles.<sup>7</sup> The difference between Figures 1 and 2 demonstrates that different concentrations of polymers have different microstructures. This is probably because the polymer molecules tend to aggregate at the surface of tiny particles or the twigs of the macromolecules at relatively high concentration while they don't aggregate



**Figure 1** AFM image of Sample 1.

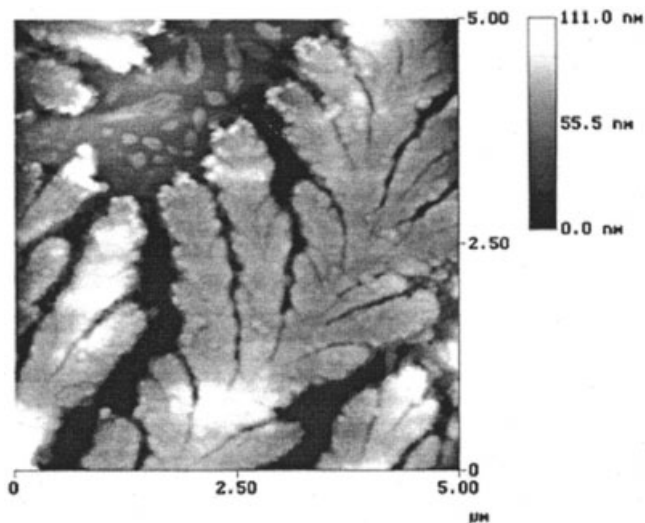


Figure 2 AFM image of Sample 2.

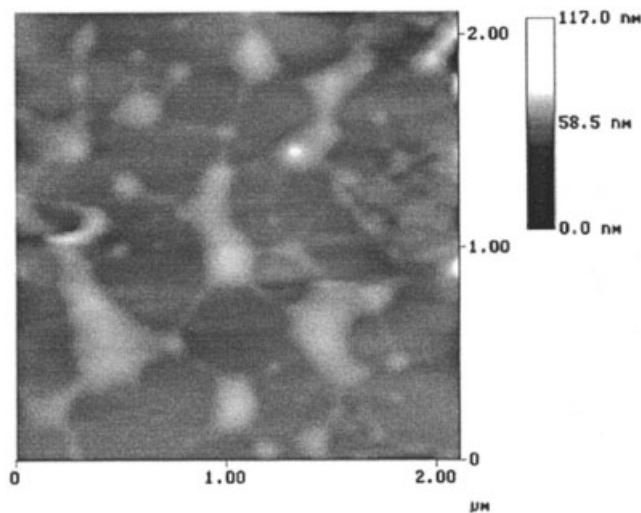


Figure 4 AFM image of Sample 4.

at low concentration. The width and the depth of the branch are  $532.9 \pm 0.15$  and  $49.9 \pm 0.3$  nm, respectively. The average diameter and the height of the tiny particles are  $61.4 \pm 0.14$  and  $7.8 \pm 0.19$  nm, respectively.

For dilute polymer systems, experimental results indicate that the polymer chains are distributed discretely before gelation. The polymer chains begin to aggregate with the increase of polymer concentration and form branch-like structures.

Figure 3 shows the AFM image of a polymer film prepared from 600 mg/L of polyacrylamide and 100 mg/L of chromium acetate. Many spherical particles and island-like structures are observed. Some particles are inlaid on the surface of the branches. The average diameter and the height of the particles are  $187.5$

$\pm 0.15$  and  $46.3 \pm 0.20$  nm, respectively. The average diameter and the height of chromium acetate particles are  $38.9 \pm 0.05$  and  $1.4 \pm 0.14$  nm, respectively.

The formation of polyacrylamide microgel is a fractal growth procedure.<sup>7</sup> The gelling system with the addition of chromium salt tends to grow at the twig of the branches. In this work, the island-like structures are also derived from the branches. The branches become thicker until some branches are merged. The change in the morphology of the polymer chains is probably due to the addition of the cross-linker that changes the composition of the solution.

#### Morphology of microgels

Sample 4 was prepared using solution with the same composition as Sample 3 but was aged at  $80^\circ\text{C}$  for 5 h. Figure 4 shows its AFM image. Some islands are formed after 5 h of aging, indicating the aggregation of polyacrylamide molecules. The length of the long axis and mini axis is  $541.8 \pm 0.13$  and  $197.8 \pm 0.13$  nm, respectively. The height is  $14.4 \pm 0.14$  nm. Many chromium acetate particles are dispersed on the surface of polyacrylamide film. The particles in Sample 4 are bigger than in Sample 3. It seems that the particles in Figure 4 are the composites of polyacrylamide and chromium acetate particles.

Figure 5 shows the AFM image of Sample 5 which contains 600 mg/L polyacrylamide and 100 mg/L chromium acetate. The sample was aged at  $80^\circ\text{C}$  for 12 h. The sample presents belt structures and spherical particles. The average diameter and the height of the particles are  $50.9 \pm 0.13$  and  $5.5 \pm 0.14$  nm, respectively, which is much bigger than the chromium acetate particles. These particles are probably the composite of polyacrylamide and chromium acetate particles. Merged islands, which are typical structures in

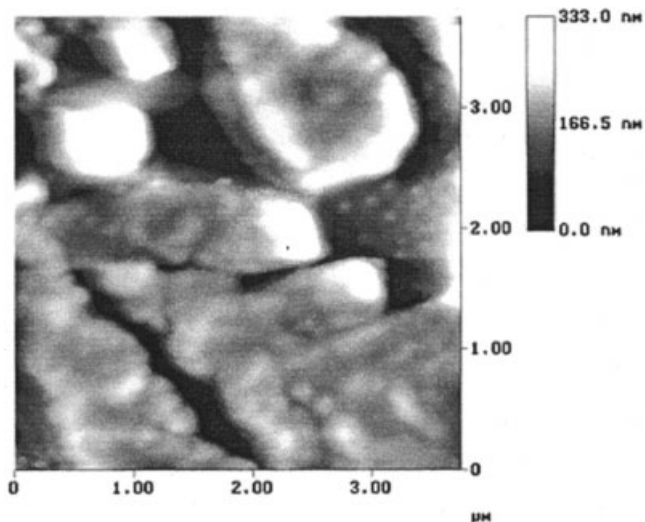


Figure 3 AFM image of Sample 3.

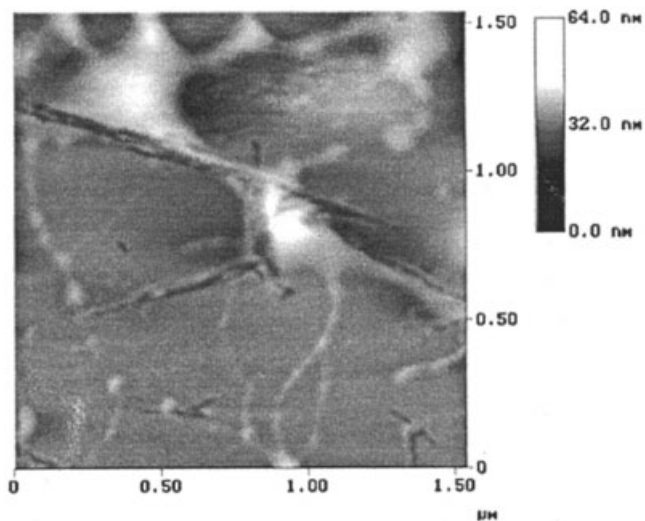


Figure 5 AFM image of Sample 5.

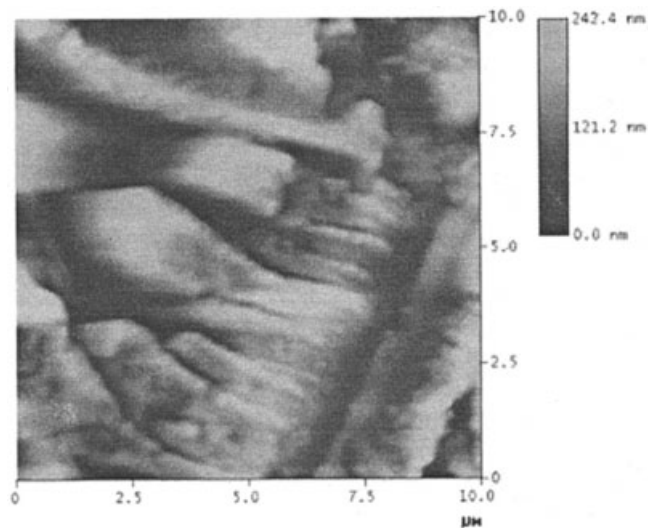


Figure 7 AFM image of Sample 7.

the gelling procedure of polyacrylamide, are also found.

Sample 6 was prepared by heating the solution containing 600 mg/L polyacrylamide and 300 mg/L chromium acetate at 80°C for 12 h. The AFM image of the film is shown in Figure 6. Flakes and belts are observed. It is also found that the increase in concentration of cross-linker results in the change of morphology of the polyacrylamide domain. Belts and flakes appear with some nanoparticles inlaid on the surface of the film.

Sample 7 was prepared by heating a mixture with the same composition as Sample 6 at 80°C for 15 days. Figure 7 shows its AFM image. Belts broader than those in Figure 6 are also observed, demonstrating compact aggregation of polyacrylamide chains. This is probably because many of chromium acetate particles

are inlaid between the polymer chains or between the monolayers. The average diameter of the particles is found to be  $88.6 \pm 0.20$  nm. According to the literature,<sup>11</sup> polyacrylamide chains are usually swollen and associated after the addition of chromium acetate. The polymer chains tend to be associated in the presence of adequate chromium particles.

Several hypotheses on the cross-linking mechanism of polyacrylamide and Cr (III) salts have been proposed.<sup>8–10</sup> Some authors suggested that the cross-linking reaction of polyacrylamide and Cr (III) salt takes place via chemical interaction of the polymer with the  $\text{Cr}^{3+}$  oligomer particles or with the colloidal  $\text{Cr}^{3+}$  hydroxide particles. The particles of chromium compounds are the reactive center. The polymer molecules agglomerate around the Cr (III) particles and the twig of the aggregate contact Cr (III) particles easily and cross-link with them. Therefore, the twigs of the aggregates grow rapidly and self-assembly fractal structures are formed. The gelation procedure, i.e., the cross-linking procedure of Cr (III) particles and polyacrylamide macromolecules, is the procedure of fractal growth. The concentration of the cross-linker influences the microstructure of the gel. When a large amount of Cr (III) ion is added, the average space between the molecules of cross-linkers is reduced and the space for chain growth is thus reduced. The polymer molecules must accumulate in a compact way. In the case of phenolic aldehyde as the cross-linker, the edges of the fractal branches are not so distinct because organic cross-linkers do not have such active centers.

Figure 8 and Figure 9 show the effects of cross-linker concentration of the morphology of polyacrylamide microgel. Sample 8 contains 600 mg/L of polyacrylamide and 600 mg/L of cross-linker. Sample 9 contains 600 mg/L of polyacrylamide and 1000 mg/L

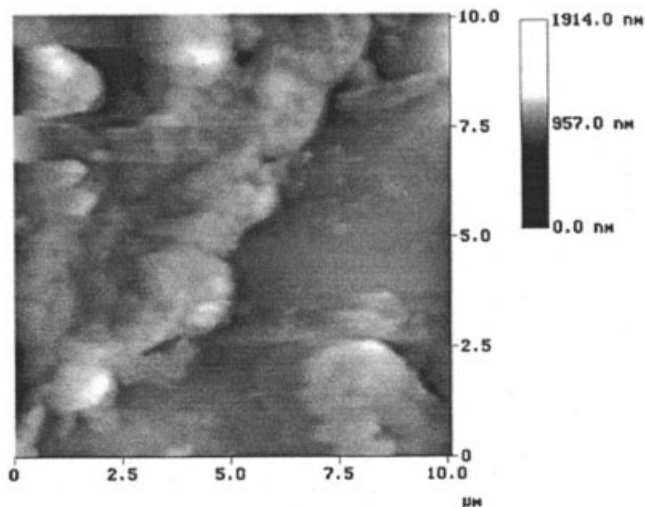


Figure 6 AFM image of Sample 6.

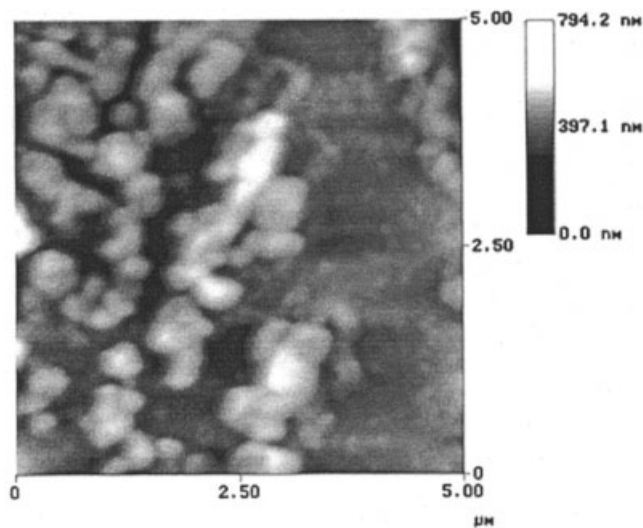


Figure 8 AFM image of Sample 8.

of cross-linker. Some nanoparticles and congeries of nanoparticles appear in the image. The average diameter of the particles is  $83.0 \pm 0.07$  nm and the height is  $17.1 \pm 0.30$  nm.

Figure 9 shows the AFM image of the 600 mg/L polyacrylamide cross-linked with 1000 mg/L phenolic aldehyde at  $80^\circ\text{C}$  for 10 days. Spherical particles and their congeries are observed. The average diameter and the height of the particles are  $275.4 \pm 0.26$  and  $104.1 \pm 0.40$  nm, respectively. The particles are bigger than those in Figure 8. It is concluded that the increase in the concentration of cross-linker can promote the aggregation of the polyacrylamide.

It is interesting to compare the AFM images of Sample 4 with that of Sample 8. The polyacrylamide chains accumulate as belts and the islands or flakes

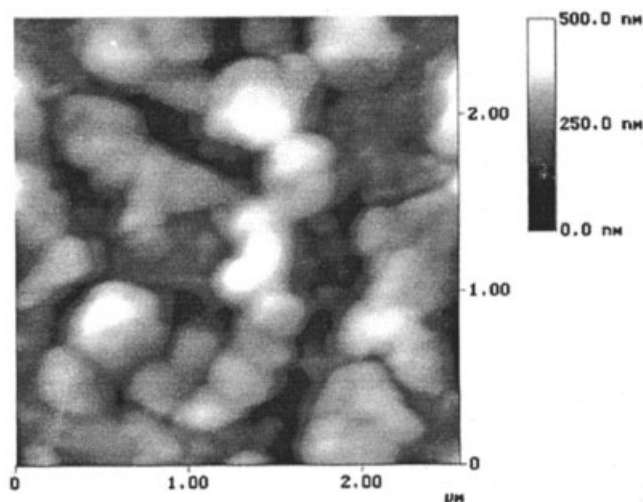


Figure 9 AFM images of the gel from polyacrylamide and phenolic aldehyde.

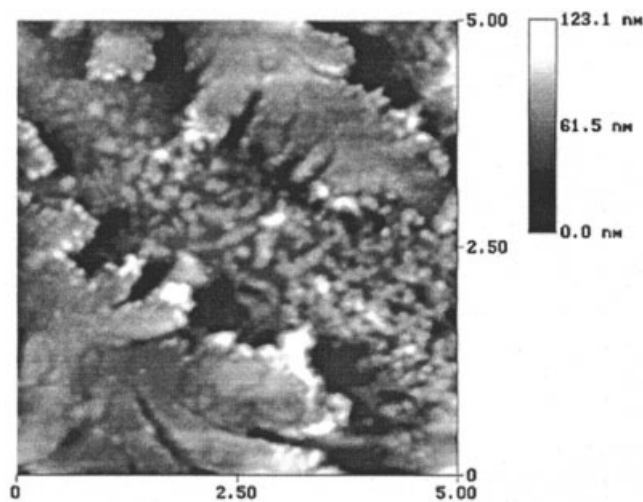


Figure 10 AFM image of Sample 10.

appear on the surface of the film when chromium acetate is used as the cross-linker. In polyacrylamide-phenolic aldehyde systems, polyacrylamide chains tend to appear as spherical particles of accumulated islands.

A 600 mg/L polyacrylamide solution was placed in a stirrer and then stirred at the rate of 10,000 r/min for 15 s. The sheared polyacrylamide solution was spread on the mica sheet until a film was formed. Figure 10 shows the AFM image of the film. Branches were still observed although they were not so integrated as those in Figure 3. Some fragments were also found. The AFM image indicated that the major part of polyacrylamide chains was reserved after shear treatment and that the fragments were broken off from the edges of the branch structures.

Tiny particles were also observed. The average diameter of the particles is  $77.5 \pm 0.26$  nm and the height is  $17.9 \pm 0.20$  nm. The possible reason for the existence of fractal branches is that the macromolecules of polyacrylamide are not completely degraded during the shear treatment. In normal cases, polyacrylamide macromolecules being sheared exhibit petaline structures. That indicates that the shear strength in our experiment was not enough to break the polymer chains completely. The irregular bright zones are probably the fragments of the polyacrylamide molecules.

In the degelation procedure, the framework of polymer molecules tends to become thinner and the viscosity of the microgel is also decreased.

Figure 11 shows the AFM image of a gelation system that contains sheared polyacrylamide and chromium acetate. Fractal branches are observed. The width and the depth of the branch are  $155.28 \pm 0.15$  and  $35.5 \pm 0.3$  nm, respectively. The size is much smaller than that in Sample 2. The polymer molecules, although being sheared, still can react with the cross-linkers and form gels.

### Variations of viscosity

A series of gel-forming fluids was prepared by mixing 600 mg/L of polyacrylamide and different cross-linkers. The variations of viscosities were recorded (see Figure 12).

As shown in Figure 12, the viscosities of the samples increased in the initial stage of gelation. For polyacrylamide–chromium acetate systems, the viscosity achieved its maximum value within 2 days. For the polyacrylamide–phenolic aldehyde system, the viscosity achieved the maximum value within 8 days. The viscosities began to decrease after reaching their maximum value. Based on the results above, the variation of viscosities can be divided into three stages: gelation stage, stable stage, and degelation stage. During the gelation stage, the viscosity increases until microgel was formed. After that, the viscosity remains stable for several days. After the stable stage, the viscosity decreases. An interesting fact was found by comparing the morphology of the gelling system with the viscosity–time curve: the viscosity increases while the polymer chains agglomerate in a relatively compact or cross-linked way. On the other hand, the viscosity tends to decrease in the degelation stage while the polymer chains accumulate in a relatively loose way. It can be concluded that the increase in viscosity is derived from high density of accumulation of polymer molecules.

The polyacrylamide being stirred at 10,000 r/min also formed a gel in this experiment, but the viscosity was much lower. This is probably because the average molecular weight of the polymer is reduced by the shear and it becomes difficult to achieve adequate intramolecular cross-linking.

In this study, the viscosity of the microgels began to decrease after 12 days of aging. The result doesn't indicate that the gelling system is unstable for field use. As a matter of fact, many stabilizers, e.g., EDTA,

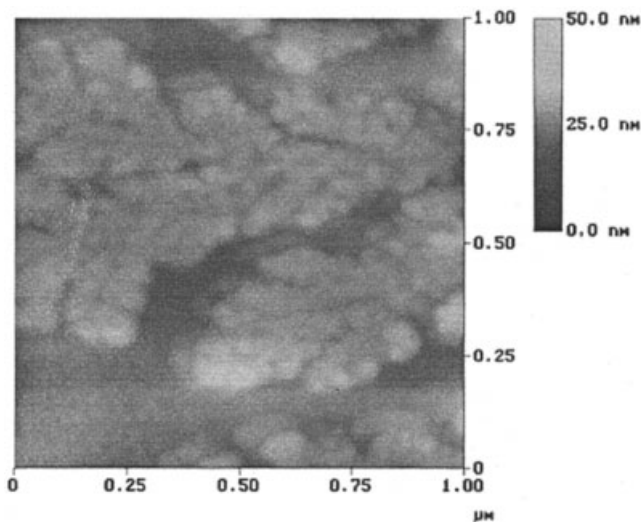


Figure 11 AFM image of Sample 11.

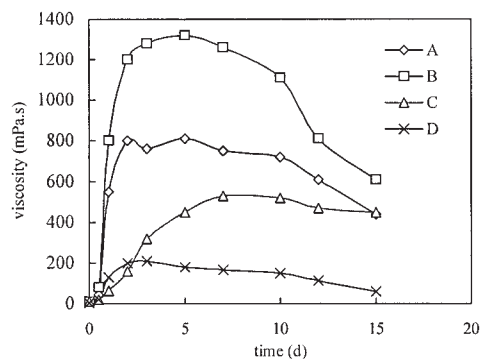


Figure 12 Variations of viscosities of gel-forming fluids and microgels: (A) 100 mg/L chromium acetate; (B) 300 mg/L chromium acetate; (C) 600 mg/L phenolic aldehyde; (D) 600 mg/L sheared polyacrylamide + 100 mg/L chromium acetate.

thiocarbamide, and hexamethylenetetramine, can be added to improve the stability of polyacrylamide gels.<sup>12</sup> In this experiment, we wished to observe the viscosity variations in a relatively short period, so the stabilizers were not employed.

### CONCLUSIONS

Polyacrylamide molecules are dispersed in solution as discrete particles at low concentration, but they aggregate as branches at relatively high concentration. The gelation procedure of polyacrylamide is a fractal growth of polymer chains. Many factors, e.g., polymer concentration, the type and concentration of cross-linker, time, and shearing, have a significant influence on the microstructure of polyacrylamide.

Relationships exist between the variations of the microstructure and that of the viscosity of polyacrylamide. The viscosity increases when the polymer chains accumulate in a compact way and the viscosity decreases when the polymer chains accumulate in a relatively loose way.

### References

- Burcik, E. J. *J Petro Technol* 1969, 4, 373–374.
- Kara, S.; Pekcan, Ö. *J Appl Polym Sci* 2001, 80, 832–830.
- Chen, Y. L.; Yuan, J. H.; Yang, W. H.; Huang, D. H.; Tan, H.; Fei, Q. *J Disper Sci Technol* 2003, 24, 113–121.
- Dona, C. L.; Green, D. W.; Willhite, G. P. *J Appl Polym Sci* 1997, 64, 1381–1391.
- Moradi-Araghi, A. *J Petro Sci Technol* 2000, 26, 1–10.
- Zhang, X.; Huang, R. H.; Xu, X. *Acta Polym Sin* 2001, 1, 8–12.
- Tan, Z. Y.; Ma, J.; Wang, C.; Bai, C. L. *Sci China* 1999, 29, 97–100.
- Shu, P. *ACS Symp Ser* 1989, 396, 137–144.
- Albonico, P.; Burrafato, G.; Lockhart, T. P. *J Polym Sci A Polym Chem* 1992, 30, 1071–1075.
- Montanari, L.; Scotti, R.; Lockhart, T. P. *Macromolecules* 1994, 27, 3341–3348.
- Naghash, H. J.; Okay, O. *J Appl Polym Sci* 1996, 60, 971.
- Albonico, P.; Lockhart, T. *J Petro Sci Technol* 1997, 18, 61–71.