Polymer Bulletin 35, 109-113 (1995)

Polymer Bulletin

Crosslinking reaction of polyacrylamide with chromium(III)

Ming Han, Lianghe Shi, Meiling Ye, Jie Ma

Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080,
People's Republic of China

Received: 24 December 1994/Revised version: 6 March 1995/Accepted: 13 March 1995

Summary

The crosslinking of initially non-hydrolyzed polyacrylamide with chromium in its +3 valence state was investigated in this work. IR spectra showed that the gelation occurred when the polyacrylamide was hydrolyzed, which implies that the gelation should take place at elevated temperature under neutral condition. The gelation process was monitored by means of viscosity measurement. The addition of acetic acid to the system might lead to the delay of gelation, owing to the synergistic effect of chelating with Cr(III) and acidity.

Introduction

The hydrogels formed from polyacrylamide and chromium are among the polymeric gels most commonly used in petroleum industry to modify the waterflooding efficiency(1). Such an application involves the injection of a mixture of the polymer and chromium aqueous solutions into the desired subterranean formations, followed by in-situ gelation. So, much attention has been paid to the understanding and controlling of the reaction. In the early work, chromium was introduced in the +6 valence state ($K_2Cr_2O_7$) and was subsequently converted to the +3 valence state by a reducing agent like thiourea. Cr(III) might then react with the polyacrylamide to form a gel at a relatively slow reaction rate(2,3). Because of the toxicity of the chromium in its +6 valence state, great efforts have been devoted in recent years to the crosslinking of polyacrylamide directly with Cr(III)(4-7).

We have reported recently the experimental investigation on the sol/gel diagrams for polyacrylamide/Cr(III) system(8). The results indicated that the hydrolysis of amide groups of the non-hydrolyzed polyacrylamide plays an important role in the gelation. Here, we present infrared spectra from which we can deduce the reaction process. By means of viscosity measurement, we show that even for the initially non-hydrolyzed polyacrylamide the crosslinking is too rapid at elevated temperature and may be delayed by the addition of acetic acid.

Experimental

A commercial polyacrylamide (No.6 Chemical Factory at Fusun, China) was used in this work. The product was non-hydrolyzed (degree of hydrolysis was inferior to 1%) with a weight-average molecular weight of 3.6×10^6g mol^{-1} . The stock polymer solutions were prepared by gentle stirring by magnetic stirrer in distilled water containing 5×10^{-3}g ml^{-1} NaCl. The stock solution of Cr(III) with a concentration of 2×10^{-3}g ml^{-1} was prepared from $CrCl_3.6H_2O$, chemical grade.

Infrared spectra of samples were recorded with IFS-113V FT-IR spectrophotometer (Bruker). Viscosity measurement was carried out with NDJ-1 rotational viscometer (Shanghai Balance Instrument Factory). The shear rate was fixed at 0.2 s^{-1} and the temperature was controlled in a water bath with a deviation of ±0.5°C.

Results and discussion

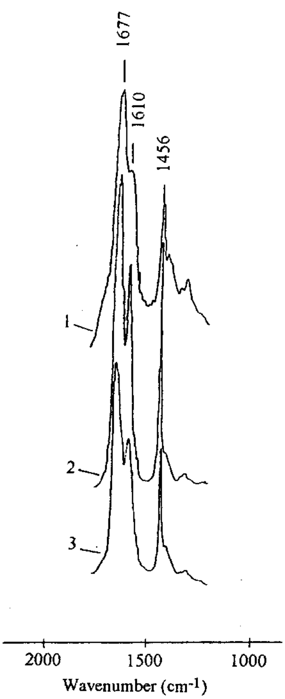
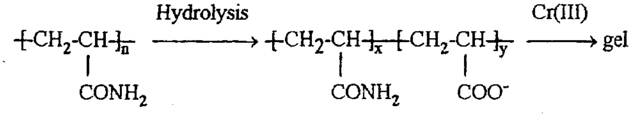


Fig.1. Infrared Spectra of Polyacrylamides
1 - non-hydrolyzed polyacrylamide
2 - polyacrylamide (70°C for 24 hours)
3 - polyacrylamide in the presence of Cr(III) (70°C for 24 hours)

Fig.1 shows the infrared spectra of polyacrylamide samples in the region between 1000 and 2000 cm^{-1}. As shown in the literature(9), the peak at 1677 cm^{-1} indicates the amide groups, whereas the peak of ν - OH in carboxyl group is located at 1610 cm^{-1}. Sample 1 corresponds to a non-hydrolyzed polyacrylamide, which shows a small shoulder at 1610 cm^{-1}. After 24 hours at 70°C, the peak at 1610 cm^{-1} is more significant, showing the occurrence of hydrolysis (sample 2). Furthermore, when we mix the Cr(III) with the polyacrylamide, the peak at 1610 cm^{-1} decreases (sample 3) due to the crosslinking reaction between ν - OH in carboxyl group and Cr(III). Therefore, we show schematically the gelation process as follows:



$$-[CH_2-\underset{\displaystyle CONH_2}{CH}]_n- \xrightarrow{\text{Hydrolysis}} -[CH_2-\underset{\displaystyle CONH_2}{CH}]_x-[CH_2-\underset{\displaystyle COO^-}{CH}]_y- \xrightarrow{\text{Cr(III)}} \text{gel}$$

It is known that Cr(III) reacts with carboxyl groups rather than amide groups. Some studies indicated that the crosslinking of polyacrylamide with Cr(III) involves not only a carboxyl group but also a neighboring amide group(10). Anyway, the hydrolysis of polyacrylamide is a necessary step for the gelation. As we know, the hydrolysis normally occurs in neutral medium at temperatures superior to 60°C(11). The crosslinking reaction between polyacrylamide and Cr(III) is thus expected to take place at elevated temperatures (>60°C).

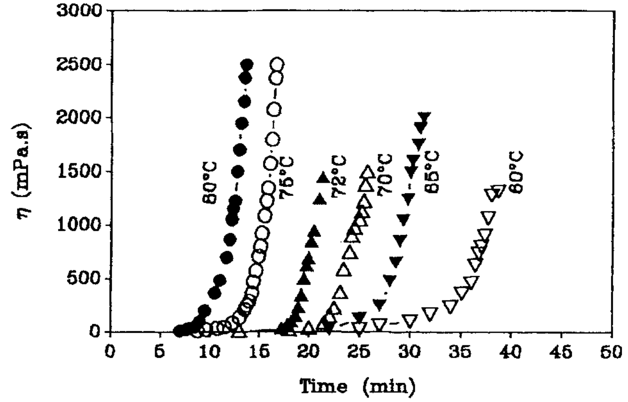


Fig.2. Variation of Viscosity with Time for Polyacrylamide/Cr(III)
conc. in polymer: 5×10^{-3}g ml^{-1}; conc. in Cr(III): 5×10^{-5}g ml^{-1}

The gelation process is monitored by means of viscosity measurement. Typical gelation curves of aqueous polyacrylamide solution in the presence of Cr(III) are shown in Fig.2. A remarkable time dependence on the apparent viscosity η is observed at the temperatures ranging from 60 to 80°C. As indicated in Fig.2, an induction period is followed by a sharp increase in the viscosity due to the gel formation. The induction period, which is usually defined as gelation time tg, becomes shorter or the gelation becomes faster with increasing temperature. For instance, tg is 36 min at 60°C, while 11 min at 80°C. From the practical point of view, the gelation seems too fast, for a treatment requires virtually a tg ranging from several hours to one day.

In order to delay the gelation rate, acetic acid was added to the system of polyacrylamide/Cr(III). The molar ratio of acetic-acid/Cr(III) was 3:1 and the initial pH was about 4. Fig.3 presents the gelation curves at temperatures ranging from 70 to 90°C. The gelation is also dependent on the temperature. It is clearly shown that the gelation was delayed in contrast to the system in the absence of acetic acid. The delay of gelation is due to the metal chelate (Cr(III)-acetate). Otherwise, the gelation rate increases with increasing pH(7). The synergistic effect of acetate groups and low pH makes the system available at a temperature up to 90°C.

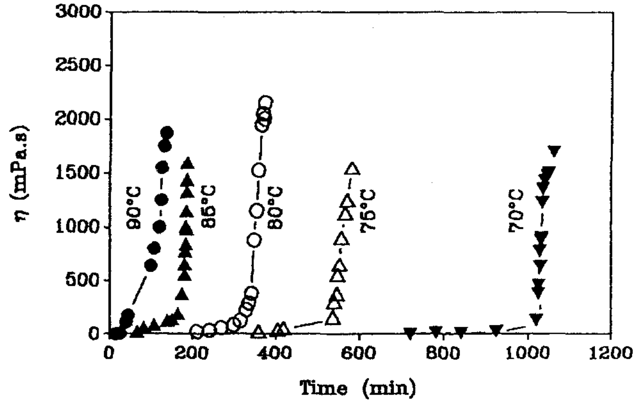


Fig.3. Variation of Viscosity with Time for Polyacrylamide/Cr(III) in the Presence of Acetic Acid
conc. in polymer: 5×10^{-3}g ml^{-1}; conc. in Cr(III): 5×10^{-5}g ml^{-3}

Jordan *et al.* developed an Arrhenius-type equation with an assumption that for a given initial composition, the proportion of the rate-controlling species that has reacted at the gelation point is the same at all temperatures(12). The Arrhenius-type equation is expressed as follows:

$$\ln t_g = \ln K + \Delta Ea/RT \qquad (1)$$

in which, K represents a constant, ΔEa the apparent activation energy, R the ideal gas constant and T the absolute temperature. In Fig.4, ln tg is plotted against T^{-1}. The linear relationship is shown for the two systems, confirming the validity of the application of the eq.(1). From the slope of the straight line, the values of ΔEa are calculated: 62.5kJ.mol^{-1} and 124.3 kJ.mol^{-1} for Polyacrylamide/Cr(III) and Polyacrylamide/Cr(III)/Acetic-acid, respectively. The increase of the apparent activation energy with the addition of acetic acid results from the chelate between Cr(III) and acetate, which makes a greater potential energy barrier for the gelation between polyacrylamide and Cr(III). It is also suggested that the addition of acetic acid to the system is an effective way to delay the gelation.

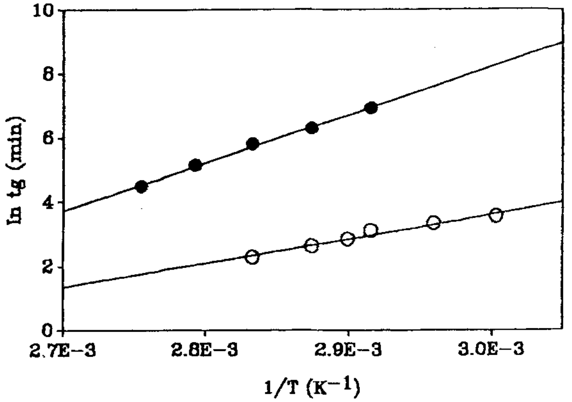


Fig.4. Logarithm of t_g versus the Reciprocal of the Absolute Temperature for • Polyacrylamide/Cr(III) and o Polyacrylamide/Cr(III)/Acetic-Acid

References

1. Needham RB, Threkeld CB, Gall JW (1974) Soc. Pet. Eng. paper 4747, the SPE-AIME Symp. on Improved Oil Recovery, Tulsa, OK, April 22-24
2. Terry RE, Huang CG, Green DW, Michnick MJ, Willhite GP (1981) Soc. Pet. Eng. J., 4: 229
3. Prud'homme RK, Uhl LT, Poinsatte JP, Halverson F (1983) Soc. Pet. Eng. J. , 8: 804
4. Allain C, Salome L (1987) Macromolecules, 20: 2957
5. Mumallah NA (1988) Soc. Pet. Eng. Reservoir Eng., 3: 243
6. Syndansk RD (1990) Soc. Pet. Eng. paper 20214, the SPE/DOE 7th Symp. on Enhanced Recovery, Tulsa, OK, April 22-25
7. Lockhart TP, Albonco P, Burrafato G (1991) J. Appl. Polym. Sci., 43: 1527
8. Han M, Shi L, Ye M, Muller G, accepted by Chinese J. Polym. Sci.
9. Muller G, Laine JP, Fenyo JC (1979) J. Appl. Polym. Sci.,17: 659
10. Burrafato G, Albonico P, Bucci S. Lockhart TP (1990) Makromol. Chem., Macromol. Symp., 39: 137
11. Muller G (1981) Polym. Bulletin, 5: 31
12. Jordan DS, Green DW, Terry RE, Willhite GP (1982) Soc. Pet. Eng. J., 8: 463