

Deformation of Linked Polymer Coils*

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Abstract Linked polymer solution (LPS) is defined as the solution of linked polymer coils (LPCs) dispersed in water, composed of low concentration partially hydrolyzed polyacrylamide (HPAM) and aluminum citrate (cross-linker). In the work, the conformational changes of LPCs under different conditions were investigated by the methods of membrane filtering under low pressure, dynamic light scattering and core flooding experiments. The results showed that in some conditions the LPCs could be compressed mechanically to 1/158.5 of their original volume because of relatively lower HPAM cross-linking. The hydration property of LPCs was similar to that of normal polymer coils. The deformation of LPCs was more restricted than that of ordinary polymer coils under the flow shear stress or the shift of hydration equilibrium caused in the variation of the electrolyte concentration which is responsible for the effective plugging in the throats of porous media when LPCs are used for deep diverting.

Keywords partially hydrolyzed polyacrylamide, linked polymer solution, coil, deformation

1 INTRODUCTION

The conformation of polymer molecules dispersed in polymer solution depends on the flexibility of macromolecular chains, interactions between macromolecules and solvent, and external conditions, *etc.* The flexibility of macromolecular chains is dependent upon the structure of the main and side chains of macromolecules and length of the main chain. If there is any change in macromolecular structure due to cross-linking reactions, the conformation of the polymer molecules changes consequently. For a linked polymer solution (LPS) with low polymer concentration, the variation in conformation of linked polymer molecules, *i.e.*, linked polymer coils are of importance in many practical applications.

Linked polymer solution is defined as the aqueous solution of cross-linked dispersed polymer coils (LPCs), consisting of partially hydrolyzed polyacrylamide (HPAM) of low concentration (usually below $0.300 \text{ g}\cdot\text{L}^{-1}$) and aluminum citrate (AlCit), the cross-linker^[1]. LPS system had been successfully applied to crude oil production as an in-depth profile control agent^[2-9] due to its low viscosity, suitable flow property and plugging ability to throats of pores in reservoir. Up to date, however, the mechanism of the plugging of the throats in porous media by LPCs is not clear, and it is believed that the plugging behavior should be related to the conformation of LPCs, on which few work was reported. By this work, three methods were developed to study the deformation behavior that may macroscopically represent conformation of LPCs: the shearing deformation property by micro-filtration experiments, the hydrating deformation by measuring the size of LPCs with dynamic light

scattering (DLS), the mechanical compression deformation by core flooding experiments.

2 EXPERIMENTAL

2.1 Materials and sample preparation

HPAM: Daqing Chemical Factory (China), relative viscosity average molecular mass M_v $(1.1-1.4)\times 10^7$, hydrolysis degree 25.8%, purified before use.

Cross-linker aluminum citrate (AlCit): self-synthesized in the laboratory.

Water: deionized and filtrated through a filter with pore size of $0.22 \mu\text{m}$.

NaCl: Beijing Shuanghuan Chemical Factory, >99.5%, GC grade.

Except for the core flooding experiments, linked polymer solutions were prepared by mixing the polymer solution with cross-linker solution at room temperature and the mixture was kept at 40°C for 7 days for the cross-linking reaction to take place fully. The concentrations of the polymer and NaCl in LPS were $0.100-0.300 \text{ g}\cdot\text{L}^{-1}$ and $0.500-2.00 \text{ g}\cdot\text{L}^{-1}$, respectively. The mass ratio of polymer to Al was 20:1. All solutions were prepared in a dust-free working cabinet.

2.2 Micro-filtration

The schematics of the micro-filtration device and the filtration membrane holder were shown in Figs. 1(a) and (b). The micro-porous membrane used was nuclear pore membrane (China Atomic Energy Institute) with average pore diameter of $1.2 \mu\text{m}$, number of the pores per square centimeter of $(4-5)\times 10^6$, and thickness of $9-10 \mu\text{m}$.

To study the conformational variation of LPCs, the LPS solution was first diluted to avoid agglom-

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eration of LPCs, and filtrated at the pressure difference of 2 kPa at room temperature. After dilution with deionized water and brines with different NaCl concentrations the concentration of HPAM in LPS was changed from $0.200 \text{ g}\cdot\text{L}^{-1}$ to $1.00 \times 10^{-4} \text{ g}\cdot\text{L}^{-1}$ or $1.00 \times 10^{-3} \text{ g}\cdot\text{L}^{-1}$. The filtration time was indexed by the interval needed by 1 ml diluted LPS passing through the membrane. The total volume of the diluted LPS was 10–20 ml.

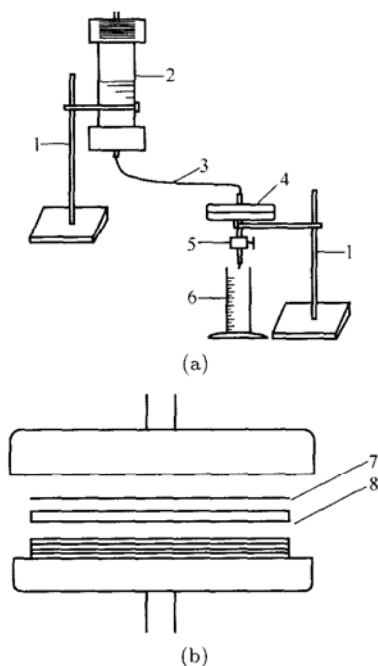


Figure 1 Sketch of micro-filtration device (a) and Sketch of filtration membrane holder (b)

1—supporter; 2—container; 3—pipe;
4—filtration membrane holder; 5—valve;
6—measuring cylinder; 7—nuclear pore membrane;
8—filtration membrane bolster

2.3 Dynamic light scattering

Dynamic light scattering measurements were carried out on a Zetasizer 2000HS PCS V1.4 (Malvern Instruments Ltd.) coupled with a 7132 Malvern photon correlator. A 10 mW helium-neon laser (wave length in vacuum $\lambda = 633 \text{ nm}$) was used as the incident beam. The angle for intensity measurements was 90° . All measurements were carried out at 25°C . Prior to the preparation the cross-linker and NaCl solutions were filtrated through a $0.22 \mu\text{m}$ filter and centrifuged at the speed of $(1.1\text{--}1.2) \times 10^4 \text{ r}\cdot\text{min}^{-1}$ for 30 minutes.

2.4 Core flooding

Core flooding equipment and experimental procedure could be referred to the Ref. [10]. The cores used

in experiments were artificially consolidated cores and attributed by Huabei Oilfield (China), the parameters of cores were shown in Table 1.

Two ways of injection were used here and described as follows:

(1) After reacted with the cross-linker for 48 h at 40°C , LPS with HPAM concentration of $0.150 \text{ g}\cdot\text{L}^{-1}$ was injected into core 1. The velocity of injection was $0.8 \text{ cm}^3\cdot\text{min}^{-1}$. Until the pressure difference rose sharply, the injection was switched to water. When the pressure difference went down to a steady level, the injection was stopped.

(2) After reacted with the cross-linker for 8 h at 40°C , LPS with HPAM concentration of $0.300 \text{ g}\cdot\text{L}^{-1}$ and water were injected alternatively to allow $5V_p$ liquid through core 2, where V_p is the volume of core 2. The velocity of injection was $0.6 \text{ cm}^3\cdot\text{min}^{-1}$. The total LPS volume injected was $70.4V_p$ in this experiment.

LPS was sampled on the exit of the core at an interval of every $0.5\text{--}1 V_p$ LPS injected. The concentrations of HPAM and Al(III) in the samples were measured by UV spectrography and an atomic absorption spectrography, respectively.

3 RESULTS AND DISCUSSION

3.1 Shearing deformation of LPCs

Figure 2 showed that about one minute was needed for 20 ml of HPAM solution of $0.0500 \text{ g}\cdot\text{L}^{-1}$ to pass through the $1.2 \mu\text{m}$ nuclear pore membrane at pressure difference 2 kPa (curve 1). In the solution, the concentration of NaCl was $2.00 \text{ g}\cdot\text{L}^{-1}$. Under the same conditions, more than 12 minutes were needed by 15 ml of the LPS with HPAM concentration of $1.00 \times 10^{-4} \text{ g}\cdot\text{L}^{-1}$ (curve 2). Before dilution, the concentration of the polymer in the LPS was $0.200 \text{ g}\cdot\text{L}^{-1}$.

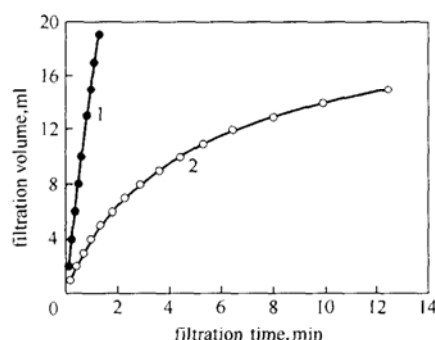


Figure 2 Filtration volume vs. filtration time curve
1—HPAM; 2—LPS

Table 1 Parameters of the cores used in flooding experiments

Core	Length, cm	Sectional area, cm^2	Pore volume, cm^3	Porosity, %	Permeability, μm^2	Dry mass, g
1	7.22	3.94	8.80	30.9	2.83	61.11
2	6.86	4.16	8.99	31.5	2.48	61.42

The results showed that the plugging ability of LPS to the membrane was much stronger than that of polymer solution, even the concentration of the HPAM solution was 500 times higher than that of the diluted LPS and the viscosity of the HPAM solution was higher. This phenomenon proved that the deformation of the LPCs and the polymer coils caused by flowing shear was different. It seemed that the polymer coils (HPAM) could be stretched and distorted more easily to pass through the membrane. The LPCs were more rigid than the polymer coils and the deformation of LPCs was more restricted. The main reason for the difference in the deformation between LPCs and the polymer coils was that LPCs were structured by the cross-linker. The LPCs with restricted deformation could be bridged easily to plug the micro-pores of the membrane.

3.2 Hydrating deformation of LPCs

LPS with $0.200 \text{ g}\cdot\text{L}^{-1}$ HPAM and $0.500 \text{ g}\cdot\text{L}^{-1}$ or $2.00 \text{ g}\cdot\text{L}^{-1}$ NaCl were used for cross-linking reaction. After that samples were diluted by brine with different concentrations of NaCl to get the samples for DLS measurements and filtration experiments.

The average hydrodynamic radii (R_h) of the LPCs in the diluted LPS were measured by DLS. The concentrations of HPAM and NaCl in the samples were shown in Table 2. After dilution, the concentrations of the electrolyte in sample D11 and sample D22 remained constant, but the concentration of sample D12 was increased to 4 times that before dilution, and the concentration of sample D21 was decreased to one fourth that before dilution. The results indicated that compared with the sample D11, R_h of the LPCs in the sample D12 became smaller. Compared with the sample D22, R_h of the LPCs in the sample D21 became larger.

The concentrations of HPAM and Al(III) in the LPS used in the filtration experiments were shown in Table 3. Fig. 3 showed that after dilution, when the concentration of NaCl in the sample F12 was in-

creased, compared with the sample F11 in which the concentration of NaCl remained constant, the time for the same volume of LPS to pass through the membrane was decreased. It indicated that the size of the LPCs in the sample F12 became smaller.

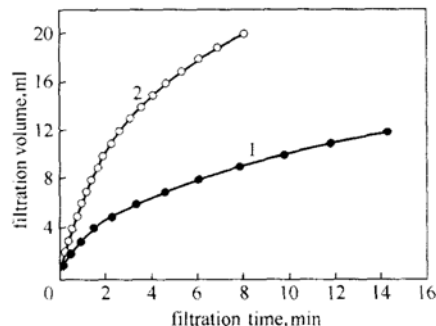


Figure 3 Filtration volume vs. filtration time curve
1—sample F11; 2—sample F12

Figure 4 showed that after dilution, when the concentration of NaCl in sample F21 was decreased, compared with sample F22 in which the concentration of NaCl remained unchanged, the time for the same volume of LPS to pass through the membrane was increased. It indicated that the size of the LPCs in sample F21 became larger.

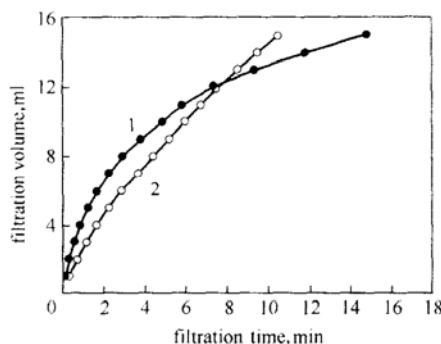


Figure 4 Filtration volume vs. filtration time curve
1—sample F22; 2—sample F21

Table 2 Average hydrodynamic radii (R_h) of the LPCs

Sample	Concentrations for cross-linking reaction, $\text{g}\cdot\text{L}^{-1}$		Concentrations after dilution for DLS experiments, $\text{g}\cdot\text{L}^{-1}$		R_h , nm
	HPAM	NaCl	HPAM	NaCl	
D11	0.200	0.500	0.100	0.500	450
D12	0.200	0.500	0.100	2.00	359
D21	0.200	2.00	0.100	0.500	326
D22	0.200	2.00	0.100	2.00	246

Table 3 Concentrations of HPAM and NaCl of the LPS used in filtration experiments

Sample	Concentrations for cross-linking reaction, $\text{g}\cdot\text{L}^{-1}$		Concentrations after dilution for filtration experiments, $\text{g}\cdot\text{L}^{-1}$	
	HPAM	NaCl	HPAM	NaCl
F11	0.200	0.500	1.00×10^{-3}	0.500
F12	0.200	0.500	1.00×10^{-3}	2.00
F21	0.200	2.00	1.00×10^{-3}	0.0100
F22	0.200	2.00	1.00×10^{-3}	2.00

These results were similar to those obtained in the DLS experiments shown in Table 2. It indicated that the size of the LPCs could be changed with the change in electrolyte concentration in the diluted LPS.

HPAM is a kind of anionic polyelectrolyte. The polymer molecules will be ionized in the solution, and carboxyl groups on the chains of HPAM will make the polymer molecules charged. The counter-ions in the solution will move to the charged groups and surround to the polymer molecules to form an electric double layer.

There is a strong attraction in the system between the charged groups and polar groups such as amide and carboxyl groups of polymer molecules, and water molecules, and then there is a hydration layer around the polymer molecules. The effect of the hydration layer makes the polymer coils incompact.

When the concentration of electrolyte is lower in the solution, the ζ potential of polyelectrolyte is higher, and the repulsion force of the charged groups with same charge on the main chain of the polymer molecule is stronger, and the hydrating layer is thicker^[11,12]. In this condition the LPCs is more incompact and the size of the LPCs is larger.

When the concentration of electrolyte in the diluted LPS is increased, the ζ potential of polyelectrolyte is decreased, and the electrostatic repulsion force among the poly-electrolytes is weakened, and the hydration extent of the LPCs is weakened too. All these reasons make the polymer molecules more compact, and the size of the LPCs becomes smaller. When the concentration of electrolyte in the diluted LPS is decreased, the results will be opposite. In other words, after the LPCs have been formed, the variation of the concentration of electrolyte in the LPS results in the variation of the electrostatic repulsion and hydrating extent of the poly-electrolytes, so does the size of the LPCs.

The variation of R_h in Table 2 is easy to be explained in terms of hydrating layer and electrostatic force in line with the above theory.

It can be seen that the size of the LPCs changed rapidly with the variation of NaCl concentration in the LPS. There is no essential difference in the hydrating property between the LPCs and polymer coils. LPS shows some similar properties to ordinary polymer solution. Because the LPCs are structured by cross-linking, the deformation of the LPCs caused by the movement in the hydrating equilibrium is more restricted than that of the ordinary polymer coils.

3.3 Mechanical compression deformation of LPCs

The quantity of HAPM or Al(III) retained in the core was calculated by subtracting the quantity of HAPM or Al(III) in the effluent from the total of

HAPM or Al injected. The retention quantity of HPAM or Al(III) in the core, A_i was expressed by the mass of HAPM or Al(III) remained in per unit mass of core. The calculating formula was shown as follows

$$A_i = (c_0 \sum V_i - \sum c_i V_i) \times 10^6 / W \quad (1)$$

For the LPS with HPAM concentration of $0.300 \text{ g}\cdot\text{L}^{-1}$, the quantity of ultimate retention of HPAM in the core was $1564 \mu\text{g}\cdot\text{L}^{-1}$. The mass of the core was 61.42 g . The molecular number of HPAM ultimately retained in the core was shown as follows

$$n = \frac{61.42 \times 1564 \times 10^{-6}}{M} N_0 \quad (2)$$

In Eq. (2), the average molecular weight of LPC is 1.25×10^7 . Supposing each LPC is composed of one polymer molecule, n is the number of the LPCs ultimately retained in the core.

The total volume occupied by n LPCs that was packed compactly is as follows

$$V = n \frac{4}{3\phi} \pi (R_h \times 10^{-4})^3 \quad (3)$$

In Eq. (3), the volume of one LPC is $\frac{4}{3}\pi(R_h \times 10^{-4})^3$. ϕ expresses the ratio of the volume of n LPCs to the total volume occupied by n LPCs packed compactly. Supposing the radii of the LPCs are equal, the value of ϕ is 0.74 ^[13].

R_h of the LPCs measured by DLS was 379 nm . If the LPCs were rigid and incompressible, Eq. (3) gives the value of V as 1425 cm^3 . The pore volume of the core used was 8.99 cm^3 , and then the volume V was 158.5 times to the pore volume of the core. This result showed that the LPCs retained in the core could be enormously compressed by the flooding pressure.

In the discussion above the LPCs were supposed to be composed of one polymer molecule. When the concentration of HPAM was $0.300 \text{ g}\cdot\text{L}^{-1}$, it is possible that a LPC would be actually composed of two or more polymer molecules. The number of the LPCs might be less than the number of the polymer molecules, and then the ratio of the volume V to the pore volume of the core was less than 158.5 .

For the LPS with HPAM concentration of $0.150 \text{ g}\cdot\text{L}^{-1}$, the ratio of the quantity of ultimate retention of HPAM to Al(III) in the core was $117.2:1$. The results showed that the LPCs and the part of Al(III) which reacted with HPAM were retained in the core and could not be washed out by the consequent flooding water. The other part of Al(III) was adsorbed in the core and would be washed out of the core.

The relative segment mass of $\begin{array}{c} \text{---CH}_2\text{CH---} \\ | \\ \text{CONH}_2 \end{array}$ is 71,

and the relative segment mass of $\begin{array}{c} \text{---CH}_2\text{CH---} \\ | \\ \text{COO}^- \end{array}$ also is 71. The relative molecular mass of HPSM is expressed by M and then the number of segments on each HPAM molecule is $M/71$. Suppose the degree of hydrolysis HPAM is 25%, and then the number of segments on each HPAM molecule that can react with the cross-linker is $0.25 M/71$. It is considered generally that one AlCit molecule will react with two cross-linking groups of HPAM molecule. There are two Al(III) on each AlCit molecule, and then the mass stoichiometric ratio of HPAM to Al(III) in the cross-linking reaction is

$$2 \times \frac{M}{0.25M/71} : 2 \times 27 = 10.5 : 1 \quad (4)$$

According to the ratio of the quantity of ultimate retention of HPAM to Al(III) (117.2:1) and the mass stoichiometric ratio of HPAM to Al(III) in the cross-linking reaction (10.5 : 1), on the experimental conditions the number of cross-linked segments of HPAM molecules was 8.96% of the total number of cross-linking segments of HPAM molecules.

Considering some part of Al(III) which did not react with HPAM was retained in the core too, it was possible that the real cross-linking conversion percent was less than 8.96%. The calculating result above showed that the cross-linking conversion percent was relatively small, and the structure of the LPCs was incompact. It was reasonable that the LPCs could be compressed to distort enormously.

The conclusion can be drawn from the results that the LPCs can be enormously compressed mechanically because of relatively lower HPAM cross-linking. The hydrating property of LPCs is similar to that of the ordinary polymer coils. Because of cross-linked structure, the deformation of LPCs caused by shear or movement of hydrating equilibrium is more restricted than that of polymer coils, which contributes to the effective plugging in the throats of porous media.

NOMENCLATURE

A_i retention quantity of HPAM or Al(III) in per unit mass of core, $\mu\text{g}\cdot\text{g}^{-1}$

c_i concentration of HPAM or Al(III) of the i th effluent sample, $\text{g}\cdot\text{L}^{-1}$
 c_0 concentration of HPAM or Al(III) of input LPS, $\text{g}\cdot\text{L}^{-1}$
 M relative molecular mass of HPAM
 N_0 Avogadro constant
 n number of HPAM molecules or LPCs ultimately retained in core
 R_h average hydrodynamic radius of LPCs, nm
 V_i volume of the i th effluent sample, L
 V_p pore volume of core, cm^3
 W mass of core, g
 ϕ ratio of volume of n LPCs to total volume occupied by n LPCs packed compactly

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