Study on the Relationship between the Relative Molecular Mass of a Polymer Clay Stabilizer and the Permeability of a Tight Reservoir

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ABSTRACT: Water-sensitivity damage is inevitable during hydraulic fracturing for tight reservoir stimulation. A polymer clay stabilizer is the most effective and commonly used agent for reducing this kind of permeability damage. However, due to the small pore throat radii of tight reservoirs, polymers may be captured and detained, resulting in secondary permeability damage caused by polymer plugging. Therefore, it is necessary to clarify the matching relationship between the relative molecular mass of the clay stabilizer and the permeability of tight cores, which has not been reported yet. In response to this problem, the residual resistance factor and the permeability damage rate of PDMDAAC (poly dimethyl diallyl ammonium chloride, a kind of commonly used polymer clay stabilizer) to tight cores from Xinjiang Oilfield were investigated in cores with permeabilities of 0.10 × 10⁻³ µm² (0.08–0.17 × 10⁻³ µm²), 0.05 × 10⁻³ µm² (0.035–0.065 × 10⁻³ µm²), and 0.01 × 10⁻³ µm² (0.007–0.020 × 10⁻³ µm²) through flow experiments. It was found that the relative molecular masses of PDMDAAC, which did not cause obvious core permeability damage, should be less than 10 000, 5000, and 2000, respectively. In addition, the bridging flocculation principle between the hydrodynamics radius of the clay stabilizer and the radius of the tight core pore throat can be used to explain the matching relationship between the relative molecular mass of the polymer clay stabilizer and the permeability of the tight reservoir. This study points out the direction for the optimization of the polymer clay stabilizer used in tight reservoir hydraulic fracturing and provides some references for the construction of hydraulic fracturing fluid systems for the efficient development of unconventional oil and gas resources.

1. INTRODUCTION

Oil and gas are indispensable fossil fuels for human beings’ life and industrial development. With the continuous growth of global oil and gas demand, more and more countries gradually shift their focus to the exploration and development of unconventional oil and gas resources.1,2 Tight oil and gas, which are kind of unconventional oil and gas reserves, refer to hydrocarbons buried in tight reservoirs, which are characterized by the permeability equal to or less than 0.1 × 10⁻³ µm².3,4 Because of their low permeability, hydraulic fracturing is the most important stimulation technology to improve oil and gas production.5,6 However, the invasion of fracturing fluids into the reservoir rocks will cause permeability damage to the tight reservoir matrix, such as water-sensitivity damage and water-locking damage.

Water-sensitivity damage refers to the phenomenon of the swelling and migration of clay minerals caused by the invading fluid, which blocks the channels for oil and gas transportation and reduces the matrix permeability.7 This type of damage is often caused by the improper selection of the working fluid, such as fracturing fluids or flooding fluids.9,10 Clay stabilizers, or clay inhibitors, commonly used chemicals to reduce water-sensitivity damage, can inhibit the hydration, swelling, dispersion, and migration of clay minerals.11 Organic cationic polymer clay stabilizers are the most widely used, most effective, and most stable clay stabilizers, mainly including polyquaternary ammonium salts, polyquaternary phosphonium salts, and polysulfide salts.12,13 Williams pointed out that an organic cationic polymer could be adsorbed on the clay particle surface through the strong electrostatic interaction. It can form multipoint adsorption with clay particles simultaneously due to the large positive charge on its surface.14 The encapsulation action of the polymer can effectively inhibit the hydration, swelling, dispersion, and migration of clay particles.15

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Yin pointed out that for reservoirs with permeabilities of 300 
Ma believed that although a cationic polymer clay stabilizer with 
by 70 
Wang pointed out that a cationic polymer clay stabilizer with 
reservoir permeability at the same time.

The research on the relationship between the reservoir pore throat and the relative molecular mass of the polymer is mostly found in polymer flooding-related literature. 

Zhu pointed out that the degree of polymer plugging in the reservoir pore throat depends on the ratio of the hydrodynamic radius ($R_h$) of the polymer to the pore throat radius ($R$). When $R_h$ is greater than $R$, the polymer coils cannot enter the pore throat and form a filter cake at the injecting face; when $R_h$ is less than 0.46$R$, the molecular clusters formed by the polymer hydration “bridge” in the pore throat of the porous medium, forming a stable triangular structure and plugging the pore throat; when $R_h$ is less than 0.46$R$, polymer molecules can also accumulate in the pore throat, but the structure is unstable and can be removed under the scouring action of the fluid. 

Yin pointed out that for reservoirs with permeabilities of $300 \times 10^{-3}$, $180 \times 10^{-3}$, and $75 \times 10^{-3} \mu m^2$, polymers with RMMs of $2000 \times 10^3$, $1500 \times 10^3$, and $1000 \times 10^3$ should be selected for polymer flooding, respectively. 

For tight reservoirs, when hydraulic fracturing is used to stimulate hydrocarbon production, it will inevitably cause water-sensitivity damage. To control this damage, the addition of a cationic polymer clay stabilizer is the most common method. However, due to the lower permeability and smaller pore throat radius of tight reservoirs, it is necessary to pay more attention to the plugging damage caused by polymer clay stabilizers in the hydraulic fracturing of tight reservoirs. The essence of solving this problem is to clarify the matching relationship between polymer clay stabilizers and the core pore throat radius. Therefore, in this study, PDMDAAC (which is a widely used cationic polymer clay stabilizer) with different RMMs and tight cores with different permeability were selected. 

The permeability of tight cores was divided into three ranges: $0.10 \times 10^{-3}$ $\mu m^2$ (within $0.08–0.17 \times 10^{-3}$ $\mu m^2$), $0.05 \times 10^{-3}$ $\mu m^2$ (within $0.035–0.065 \times 10^{-3}$ $\mu m^2$), and $0.01 \times 10^{-3}$ $\mu m^2$ (within $0.007–0.020 \times 10^{-3}$ $\mu m^2$). The matching relationship between the relative molecular mass of PDMDAAC and the permeability of tight cores was studied. Only by selecting a clay stabilizer with a suitable relative molecular mass, can the water-sensitivity damage be reduced, and the permeability damage caused by polymer plugging can be reduced, thereby further improving the stimulation effect of fracturing. The results have a guiding significance for the selection of the relative molecular mass of polymer clay stabilizers used in hydraulic fracturing stimulation of tight reservoirs and shale reservoirs, which are characterized by low permeability and high clay mineral content.

### 2. MATERIALS AND METHODS

#### 2.1. Materials

Tight sandstone cores were taken from Xinjiang Oilfield. The permeability of cores can be mainly divided into three ranges: $0.08–0.17 \times 10^{-3}$ $\mu m^2$ (recorded as $0.10 \times 10^{-3} \mu m^2$ in this study), $0.05 \times 10^{-3} \mu m^2$ (recorded as $0.05 \times 10^{-3} \mu m^2$), and $0.007–0.020 \times 10^{-3} \mu m^2$ (recorded as $0.01 \times 10^{-3} \mu m^2$). The specific parameters are shown in Table 2. The mineral analysis and clay mineral analysis of cores are shown in Figure 1. The clay stabilizers of poly dimethyl diallyl ammonium chloride (PDMDAAC) with relative molecular masses of 2428, 5243, 10 335, 25 076, and 52 821 were prepared.
The experimental steps are as follows.

Radius of PDMDAAC.

(i) A series of PDMDAAC solutions were prepared, and the mass fractions of PDMDAAC were 0.01, 0.05, 0.1, 0.3, and 0.5%. The solutions were fully stirred and stood for 24 h until the molecules of PDMDAAC were fully hydrated and stretched.

(ii) The solutions were filtered through a filter membrane with a diameter of 0.22 μm.

(iii) A laser particle size analyzer (Brookhaven BI 90-Plus/Zeta plus) was used to measure the hydrodynamic radius \(R_d\). The measurement conditions included a scattering angle of 90° and a temperature of 25 °C.

2.2. Methods

2.2.1. Determination of the Hydrodynamic Radius of PDMDAAC. The hydrodynamic radius of PDMDAAC was determined by the dynamic light scattering (DLS) method. The experimental steps are as follows.

(i) A series of PDMDAAC solutions were prepared, and the mass fractions of PDMDAAC were 0.01, 0.05, 0.1, 0.3, and 0.5%. The solutions were fully stirred and stood for 24 h until the molecules of PDMDAAC were fully hydrated and stretched.

(ii) The solutions were filtered through a filter membrane with a diameter of 0.22 μm.

(iii) A laser particle size analyzer (Brookhaven BI 90-Plus/Zeta plus) was used to measure the hydrodynamic radius \(R_d\). The measurement conditions included a scattering angle of 90° and a temperature of 25 °C.

2.2.2. Determination of the Antiswelling Rate of the Clay Stabilizer. The antiswelling rate was employed to evaluate the impact of the polymer solution on the permeability of porous media in polymer flooding. It refers to the permeability ratio of brine (usually 4% KCl solution) in cores before and after the injection of the polymer solution. Since the clay stabilizer (PDMDAAC) used in this research is also a polymer, RRF was chosen to evaluate its plugging damage to cores.

The measurement procedure is as follows.

(i) The cores were washed and dried, and the basic parameters were measured. Then, the cores were evacuated and saturated with 4% KCl brine.

(ii) 20 PV (pore volume) of KCl brine was injected from the positive direction (the direction in which the formation fluids flowed in the reservoir) to measure the initial permeability \(k_0\).

(iii) 10 PV of the clay stabilizer solution (0.5%) prepared based on the KCl brine was injected from the opposite direction (the opposite direction of the flow of formation fluids in the reservoir). Then, 20 PV of the KCl brine was injected from the positive direction to measure the core permeability after the clay stabilizer treatment \(k_1\).

(iv) RRF can be calculated according to the formula \(k_0/k_1\). The injection rate during the measurement procedure was 0.05 mL/min, and the confining pressure was 3.5 MPa.

In addition, to study the effect of the RMM of PDMDAAC on the residual resistance factor, three groups of experiments were designed to measure RRF, according to the core permeability in the laboratory. Sodium bentonite was provided by the oilfield. The simulated formation water was prepared from deionized water and inorganic salts, and the ionic composition is shown in Table 1. The simulated formation water should be filtered with a filter membrane (0.22 μm) before use. Deionized water was made in the laboratory. All of the other chemicals with the analytical grade were purchased from Sinopharm China.

Table 1. The simulated formation water should be filtered with a filter membrane (0.22 μm).

| Parameter        | Value       |
|------------------|-------------|
| Deionized water  |             |
| Sodium chloride  | 0.13 g      |
| Calcium chloride | 0.25 g      |
| Magnesium chloride| 0.08 g    |
| Sulfate          | 0.05 g      |

The simulated formation water was prepared from deionized water and inorganic salts, and the ionic composition is shown in Table 2.

Table 2. Basic Parameters of the Cores

| Parameter        | Value       |
|------------------|-------------|
| Permeability/10^3 μm² | Cores no. | length/cm | diameter/cm | porosity/% | gas permeability/10^3 μm² |
|------------------|-------------|
| 0.10 (0.08–0.17) | 0.10–1      | 3.99      | 2.52        | 8.58       | 0.14                     |
|                  | 0.10–2      | 3.82      | 2.52        | 8.61       | 0.12                     |
|                  | 0.10–3      | 3.97      | 2.52        | 8.06       | 0.13                     |
|                  | 0.10–4      | 3.79      | 2.52        | 8.82       | 0.11                     |
|                  | 0.10–5      | 3.85      | 2.52        | 8.23       | 0.12                     |
|                  | 0.10–Y      | 3.86      | 2.52        | 8.43       | 0.09                     |
| 0.05 (0.035–0.065) | 0.05–1     | 3.76      | 2.50        | 6.57       | 0.07                     |
|                  | 0.05–2      | 3.91      | 2.50        | 6.40       | 0.05                     |
|                  | 0.05–3      | 3.78      | 2.50        | 6.52       | 0.06                     |
|                  | 0.05–4      | 3.77      | 2.50        | 6.36       | 0.04                     |
|                  | 0.05–5      | 3.84      | 2.50        | 6.93       | 0.04                     |
|                  | 0.05–Y      | 3.93      | 2.50        | 6.58       | 0.06                     |
| 0.01 (0.007–0.020) | 0.01–1     | 3.81      | 2.53        | 5.34       | 0.01                     |
|                  | 0.01–2      | 3.95      | 2.53        | 4.89       | 0.01                     |
|                  | 0.01–3      | 3.89      | 2.53        | 4.24       | 0.02                     |
|                  | 0.01–4      | 3.91      | 2.53        | 4.63       | 0.02                     |
|                  | 0.01–5      | 3.82      | 2.53        | 4.26       | 0.02                     |
|                  | 0.01–Y      | 3.88      | 2.53        | 4.55       | 0.02                     |

(iii) The first step was repeated with kerosene instead of the PDMDAAC solution, and the volume of the swelling sodium bentonite was obtained \(V_0\).

(iv) The antiswelling rate was calculated according to the following formula.

\[ B = \frac{V_2 - V_1}{V_2 - V_0} \times 100\% \] (1)

where \(B\) is the antiswelling rate, %, and \(V_0\), \(V_1\), and \(V_2\) are the swelling volumes of sodium bentonite in kerosene, clay stabilizer solution, and distilled water, respectively, mL.
differences \((0.10 \times 10^{-3}, 0.05 \times 10^{-3}, \text{and} \ 0.01 \times 10^{-3} \ \mu m^2)\). The cores were numbered according to the following rules: the first number refers to the permeability range of the core \((0.10, 0.05, \text{and} \ 0.01 \) meant that the core permeability was in the range of \(0.10 \times 10^{-3}, 0.05 \times 10^{-3}, \text{and} \ 0.01 \times 10^{-3} \ \mu m^2\); respectively), the second number refers to the RMM of the PDMDAAC solution that should be injected into the cores \((1, 2, 3, 4, \text{and} \ 5 \) meant that the RMM of PDMDAAC were 2428, 5243, 10335, 25076, and 52821, respectively, and \(Y\) meant that the cores were selected for mercury intrusion capillary pressure measurement to characterize the core pore structure). The mass fraction of the PDMDAAC solution was 0.5%. The basic parameters of the cores used in these tests are shown in Table 2.

2.2.4. Determination of the Core Permeability Damage Rate. The core permeability damage rate is used to characterize the degree of water-sensitivity damage caused by the fracturing fluid. The core permeability damage rate is defined as the ratio of the degree of water-sensitivity damage caused by the fracturing fluid. The core permeability damage rate is defined as the ratio of the reduction value to the initial value of the core permeability, after the injection of extraneous fluid into the core.

The determination method is as follows.

(i) The cores were washed and dried, and the basic parameters were measured. Then, the cores were evacuated and saturated with formation water.

(ii) 20 PV of the formation water was injected from the positive direction to measure the initial permeability \((k_{0})\).

(iii) 10 PV of the clay stabilizer solution prepared with formation water was injected from the opposite direction. Then, 20 PV of the formation water was injected from the positive direction to measure the core permeability after clay stabilizer treatment \((k_{w1})\).

(iv) The core permeability damage rate can be calculated according to the formula \((k_{0} - k_{w1})/k_{w1} \times 100\%\).

3. RESULTS AND DISCUSSION

3.1. Effect of the RMM of PDMDAAC on the Residual Resistance Factor. The flow experiments were conducted to study the effect of the RMM of PDMDAAC on the residual resistance factor, and the results are shown in Figure 2.

It can be seen from Figure 2 that (i) for cores with a permeability of \(0.10 \times 10^{-3} \ \mu m^2\), when the RMM of PDMDAAC was less than 10 335, there was little change in RRF. However, when the RMM was 25 076, the RRF significantly increased (the increase rate was 47.5%). (ii) For cores with a permeability of \(0.05 \times 10^{-3} \ \mu m^2\), the RRF was small when the RMM did not exceed 5243 and increased sharply (64.5%) when the RMM was 10 335. (iii) For cores with a permeability of \(0.01 \times 10^{-3} \ \mu m^2\), when the RMM of PDMDAAC changed from 2428 to 5243, the RRF increased by 52.8%.

The above changes indicate that for cores within the same permeability range, the higher the relative molecular mass of PDMDAAC, the greater the residual resistance factor, that is, the greater the flow resistance. Moreover, for PDMDAAC with the same relative molecular mass, the lower the core permeability, the greater the residual resistance factor. Besides, the lower the core permeability, the more sensitive the residual resistance factor to the relative molecular mass of PDMDAAC.

In summary, for cores with permeabilities of \(0.10 \times 10^{-3}, 0.05 \times 10^{-3}, \text{and} \ 0.01 \times 10^{-3} \ \mu m^2\), the corresponding relative molecular masses of PDMDAAC that the residual resistance factor began to change sharply, or to say, the flow resistance started to increase significantly, were 10 335, 5243, and 2428, respectively.

3.2. Effect of the RMM of PDMDAAC on the Permeability Damage Rate. The core permeability damage rate after the injection of PDMDAAC with different RMMs is shown in Figure 3. As can be seen from Figure 3, for cores with a permeability of \(0.10 \times 10^{-3} \ \mu m^2\), when the RMMs of PDMDAAC were 5243 and 10 335, the damage rate increased to 42.53 and 60.94%, respectively. In addition, for cores with permeabilities of \(0.05 \times 10^{-3} \ \mu m^2\) and \(0.01 \times 10^{-3} \ \mu m^2\), the damage rate showed a similar change pattern when the RMM of PDMDAAC increased. Therefore, it can be concluded that when the polymer clay stabilizer is injected into the tight cores, it will cause varying degrees of damage to the core permeability, and this damage degree will increase with the decrease of core permeability and the increase of the relative molecular mass of the polymer clay stabilizer.

![Figure 2](https://doi.org/10.1021/acs.omega.2c03051)

**Figure 2.** Relationship between the residual resistance factor and the relative molecular mass of PDMDAAC.

![Figure 3](https://doi.org/10.1021/acs.omega.2c03051)

**Figure 3.** Relationship between the core permeability damage rate and the relative molecular mass of PDMDAAC.
The reasons for this permeability damage may include the following two aspects. On the one hand, because there were about 5% of clay minerals in the core, the injection of extraneous fluid will inevitably cause swelling and migration of the clay minerals, which reduce the core permeability. On the other hand, because there was polymer in the injected solution, the pore throat may be plugged if its hydrodynamic radius does not match the core pore throat, resulting in core permeability reduction.

The PDMDAAC solution could cause water-sensitivity damage to clay minerals from the perspective of its attribute of extraneous fluid, and it could also reduce the water-sensitivity damage from the perspective of its attribute of the clay stabilizer. Therefore, to find out the main causes of permeability reduction when PDMDAAC were injected, it is necessary to clarify the antiswelling properties of PDMDAAC in the first place. For this reason, the antiswelling effect of PDMDAAC with different RMMs on sodium bentonite was investigated by the centrifugal method. The experimental results are shown in Figure 4.

It can be seen from Figure 3 that PDMDAAC with different RMMs had similar clay antiswelling properties. Therefore, it can be considered that the water-sensitivity damage of PDMDAAC solutions with different RMMs should be close. Combined with the above analysis that "the reasons for this permeability damage may include the following two aspects", it can be speculated that the mismatching relationship between the hydrodynamic radius of PDMDAAC and the core pore throat is the main reason for core permeability damage. That is, when the relative molecular mass of the clay stabilizer is high, it will cause plugging damage to cores with small pore throats.

Therefore, it can be inferred from Figure 4 that for cores with permeabilities of $0.10 \times 10^{-3}$, $0.05 \times 10^{-3}$, and $0.01 \times 10^{-3} \mu m^2$, the ranges of the relative molecular masses of clay stabilizers that may cause polymer detention and pore throat plugging should be $10.335 - 25.076$, $52.43 - 103.35$, and $242.8 - 524.3$, respectively.

### 3.3. Matching Mechanism between the RMM of PDMDAAC and Tight Core Permeability

#### 3.3.1. Hydrodynamic Radius of PDMDAAC

The hydrodynamic radius of PDMDAAC with different relative molecular masses was studied, and the results are shown in Figure 5.

As can be seen from Figure 4, for PDMDAAC with RMMs of 2428, 5243, 10335, 25076, and 52821, the hydrodynamic radii were 2.88, 8.89, 18.49, 25.80, and 40.87 nm, respectively, when the mass fraction of the solution was 0.1%. However, when the mass fraction was 0.5%, the hydrodynamic radius was 3.18, 10.09, 19.29, 28.16, and 43.71 nm, respectively. From these results, two conclusions can be obtained.

(i) For PDMDAAC with the same RMM, the hydrodynamic radius increased with the increase of its mass fraction in the solution at the beginning, and then tended to be stable. The reason lies in that with the increase of the content of PDMDAAC, the probability of interpenetration and interlacing between molecule clusters increased, thus increasing its hydrodynamic radius.

(ii) In addition, in solutions with the same mass fraction, the RMM of PDMDAAC has a great influence on its hydrodynamic radius. The larger the relative molecular mass of PDMDAAC, the larger its hydrodynamic radius. The reason lies in that with the increase of the relative molecular mass, the contour length of the polymer chain becomes longer. The polymer chain is more prone to entangle with each other, which ultimately increases the polymer hydrodynamic radius.

In a word, with the increase of the relative molecular mass and the content of PDMDAAC in solution, the hydrodynamic radius of PDMDAAC molecules in solution increases, resulting in the increase of flow space required for polymer solution to flow in porous media.

#### 3.3.2. Pore Throat Characteristics of Tight Cores

The high-pressure mercury injection test has been one of the most important methods for analyzing the pore throat structures. Therefore, the matching mechanism between the RMM of PDMDAAC and tight core permeability was clarified.
Cores selected from the three permeability ranges were used in mercury intrusion capillary pressure measurement tests according to the petroleum industry standard SY/T 5346−2005 “Rock capillary pressure measurement”, through an automatic mercury intrusion apparatus (Mike Instruments AutoPore IV 9505). When mercury is injected into rock pores as a nonwetting phase, external pressure needs to be applied. The contact angle (140°), interfacial tension (480 mn/m), and pore throat radius determine the mercury injection pressure. During the mercury injection experiment, the contact angle and interfacial tension of the sample remained constant, and mercury was injected into the rock pores at a very low quasistatic mercury injection rate. According to the change of mercury injection pressure, the capillary pressure curve and the pore throat distribution ratio can be obtained, as shown in Figures 6 and 7, respectively.

![Figure 6. Capillary pressure curve of the cores with different permeabilities.](image)

The shape of the mercury injection capillary pressure curve is closely related to the core permeability and is also affected by the pore throat structure. As shown in Figure 5, with the decrease of core permeability, the mercury injection capillary pressure curve shifted to the right, indicating that the pore throat radius decreases. Besides, the distribution diagram of the core pore throat radius can be obtained through a high-pressure mercury injection capillary experiment, and the results are shown in Figure 7.

As can be seen from Figure 7, with the decrease of core permeability, the histogram of the pore throat radius shifted to the left, and the curve of permeability contribution ratio also shifted to the left. Specifically, for cores with a permeability of 0.10 × 10^{-3} μm^2, the pore throat radius was mainly concentrated in the range of 0.1600−0.0250 μm, among which the radius in the range of 0.1600−0.0400 μm accounted for 63.36% and contributed 98.64% to the core permeability. Moreover, for cores with a permeability of 0.05 × 10^{-3} μm^2, the pore throat radius was mainly concentrated in the range of 0.0630−0.0100 μm, among which the radius in the range of 0.0630−0.0250 μm accounted for 44.61% and contributed 90.25% to its permeability. In addition, for cores with a permeability of 0.01 × 10^{-3} μm^2, the pore throat radius was mainly concentrated in the range of 0.0160−0.0040 μm, among which the radius in the range of 0.0160−0.0063 μm accounted for 16.22% and contributed 92.58% to the core permeability.

According to the results of the mercury injection capillary pressure curve and the pore size distribution, the pore structure characteristics can be obtained. Three kinds of pore throat radii were selected and are listed in Table 3.

![Figure 7. Distribution diagram of the core pore size.](image)

**Table 3. Core Pore Throat Radius**

| core no.  | 0.10−Y | 0.05−Y | 0.01−Y |
|-----------|--------|--------|--------|
| maximum pore throat radius/μm | 0.2250 | 0.0775 | 0.0201 |
| average pore throat radius/μm | 0.0536 | 0.0198 | 0.0063 |
| median pore throat radius/μm | 0.0695 | 0.0245 |

It can be found in Table 3 that for cores with permeabilities of 0.10 × 10^{-3}, 0.05 × 10^{-3}, and 0.01 × 10^{-3} μm^2, all three kinds of pore throat radii (maximum pore throat radius, average pore throat radius, and median pore throat radius) showed a decreasing trend. Therefore, it can be concluded that the lower the core permeability, the smaller the characteristic parameters of the core pore throat radius.

Furthermore, the pore throat with a relatively large radius in the core accounted for only about 50%, but its contribution to permeability was up to 90%. Based on this, it can be concluded that if the pore throat with a large radius is blocked, the core permeability decreases sharply. Therefore, the cores with low permeability are more sensitive to the hydrodynamic radius of the polymer solution that flows inside.
3.3.3. Matching Mechanism Analysis. From the residual resistance factor tests and the permeability damage tests, it can be speculated that the mismatching relationship between the hydrodynamic radius of PDMDAAC molecules and the core pore throat is the main reason for the result that the core permeability damage rate changed with the RMM of PDMDAAC. To verify this speculation, the hydrodynamic radius of PDMDAAC and the pore throat characteristics of the tight core were investigated. The results (as shown in Figure 8) are as follows: (i) the hydrodynamic radii of PDMDAAC with RMMs of 25,076, 10,335, 5,243, and 2,428 were 28.16, 19.29, 10.09, and 3.18 nm, respectively, when its mass fraction was 0.5% and (ii) the average pore throat radii of tight cores with permeabilities of $0.10 \times 10^{-3}$, $0.05 \times 10^{-3}$, and $0.01 \times 10^{-3}$ μm$^2$ were 53.6, 19.8, and 6.3 nm, respectively.

By comparing the hydrodynamic radius of PDMDAAC with the average pore throat radius, it can be seen that the experimental results meet the “bridging flocculation principle” used in polymer flooding. The plugging degree of the reservoir pore throat depends on the relationship between the hydrodynamic radius of the polymer and the reservoir pore throat radius. When the ratio of the hydrodynamic radius to the pore throat radius is greater than 0.46, the polymer coils formed by the hydration molecules of PDMDAAC bridge in the pore throats, forming a stable triangular structure and plugging the pore throats.

The molecular clusters of PDMDAAC in an aqueous solution can be observed by a transmission electron microscope (JEM 2100F, Japan Electronics Co., Ltd.), as shown in Figure 9. It can be found that PDMDAAC molecules aggregate together through intermolecular interactions. Some of them exist in a spherical aggregation form, while others exist in a strip form, which increases the molecular clusters and further enhances the bridging performance. In addition, the dimensional data shown in Figure 8 can also further verify the hydrodynamic radius of PDMDAAC in an aqueous solution. Therefore, the mismatching relationship between the hydrodynamic radius of PDMDAAC and the pore throat radius is the main reason for the damage of the PDMDAAC solution to tight cores.

Because the hydrodynamic radius of PDMDAAC is closely related to its relative molecular mass, PDMDAAC with different RMMs has different behaviors when entering the pore throat: (i) For the PDMDAAC solution with a low RMM value, the polymer can move freely in the pore throat and can be adsorbed quickly on the surface of clay minerals, thus showing the clay antischwell effect. (ii) For the PDMDAAC solution with a high RMM value, the polymer molecules are captured and detained in the pore throat due to its longer molecular chain and larger hydrodynamic radius, thus plugging the pore throat. (iii) In addition, as the injection volume increases, the number of blocked pore throats also increases. The PDMDAAC molecular clusters may even be filtered out and detained on the end face of cores, forming a thin film covering the end face of the core, as shown in Figure 10. The plugging caused by bridging flocculation of PDMDAAC affects the permeability of the reservoir matrix on the one hand and reduces the effective content of the clay stabilizer in the matrix pores on the other hand so that the antischwell effect of PDMDAAC on clay
minerals cannot be fully exerted, resulting in serious water-sensitivity damage.

Based on the above mechanism analysis, it can be seen that the mismatching relationship between the hydrodynamic radius and the core pore throat radius is the main reason for the damage of PDMDAAC to tight cores. Therefore, the mismatching relationship between the relative molecular mass of the polymer clay stabilizer and the pore throat radius of the tight reservoir should be fully considered when selecting the clay stabilizer for tight reservoir hydraulic fracturing. The clay stabilizers with lower relative molecular masses should be selected as far as possible, on the premise of meeting the requirements of the antiswelling effect for clay minerals.

In addition, it also can be seen that (i) for tight cores with permeabilities of $0.10 \times 10^{-3}$, $0.05 \times 10^{-3}$, and $0.01 \times 10^{-3}$ $\mu m^2$, the relative molecular masses when the residual resistance factor begins to change significantly are $10 \ 335$, $5243$, and $2428$, respectively. (ii) The relative molecular mass ranges when the obvious detention and plugging damage occurred were $10 \ 335$–$25 \ 076$, $5243$–$10 \ 335$, and $2428$–$5243$. Therefore, for tight cores, obtained from Xinjiang Oilfield, with permeabilities of $0.10 \times 10^{-3}$, $0.05 \times 10^{-3}$, and $0.01 \times 10^{-3}$ $\mu m^2$, the relative molecular masses of the polymer clay stabilizer used in fracturing fluid should be lower than $10 \ 000$, $5000$, and $2000$, respectively, so as to prevent the plugging damage of the clay stabilizer and ensure the fracturing effect.

4. CONCLUSIONS

Aiming at the problem of the permeability damage caused by the polymer clay stabilizer to the tight reservoir, the relationship between the relative molecular mass of PDMDAAC and the permeability of tight cores was studied, and the following conclusions can be obtained.

When the unsuitable relative molecular mass of the polymer clay stabilizer was selected, it was captured and detained at the core pore throat, resulting in damage to tight core permeability. Taking the residual resistance factor and the permeability damage rate as the evaluation parameters, the mismatching relationship between the relative molecular mass of PDMDAAC and the core pore throat radius was studied, and it was proved to be the main reason for the permeability damage of the polymer clay stabilizer to the tight reservoir. In addition, for Xinjiang Oilfield tight cores with permeabilities of $0.10 \times 10^{-3}$, $0.05 \times 10^{-3}$, and $0.01 \times 10^{-3}$ $\mu m^2$, the relative molecular masses of PDMDAAC, which will not cause obvious polymer plugging damage, should be lower than $10000$, $5000$, and $2000$, respectively.

![Figure 10. SEM images of PDMDAAC captured and detained on the core end surface.](https://pubs.acs.org/10.1021/acsomega.2c03051)

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**Notes**

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