Experimental Investigation on a Novel Polyelectrolyte Molecular Deposition Film for Improved Injectivity in Low-Permeability Reservoirs

Nanjun Lai,* Xintong Nie, Xu Zheng, Wensen Zhao, Xubin Zhao, and Yong Wang

ABSTRACT: Acrylamide and dimethyl diallyl ammonium chloride were used as monomers to synthesize a polyelectrolyte molecular deposition film (PMDF) injection agent for solving the problem of high injection pressure of water wells in low-permeability reservoirs. The structure of the PMDF injection agent was determined through IR and $^1$H nuclear magnetic resonance (NMR). The performance evaluation results show a change of wettability from hydrophilic to neutral wetting with the contact angle changing from 22.32° to 73.31° because of agent injection. It can also change the negative $\zeta$-potential on the surface of the sand to a positive value. For comparison, core displacement experiments involving the commercial Gemini surfactant DF-G reveal that the effects of the depressurization of PMDF are more obvious than those of DF-G. The adsorption stability of the former is better than that of the latter. Especially, under a high-speed water flow of 30 pore volume (PV) injection, the depressurization rate of PMDF is still as high as 43.59%. Finally, the oil−water relative permeability curves and core nuclear magnetic resonance (NMR) experiments demonstrate that the PMDF treatment can reduce the irreducible water saturation, which indicated that the porosity of the flowable part of the core increased and the swept volume was increased. The suitable range of PMDF according to NMR pore-radius distribution within a low-permeability reservoir: the flowable partial pore required the throat radius greater than 0.01 $\mu$m.

1. INTRODUCTION

The remaining oil resources in China are seriously deteriorating with complex surface and underground conditions.¹ In recent years, the newly proven reserves of oil have tended to decline, and the proportions of low-permeability and extra-low-permeability reserves in new geological reserves increase yearly. Furthermore, 73% of the remaining resources have low permeability.²,³ Low-permeability reservoirs have low natural energy, and reservoir development generally adopts conventional water injection.⁴ However, these reservoirs have fine pore throats, complicated structures, and extremely poor seepage capacity.⁵ Therefore, the high injection pressure and poor ability of injection are universal problems in the water flooding of low-permeability reservoirs.⁶ Efficient chemical agents for depressurization and increasing injection have been widely explored and developed in the field of oilfield chemistry.

Chemical depressurization and increasing injection have been extensively studied. Two main technologies have been explored: reservoir reconstruction and surface modification. The reservoir reconstruction technology is applied to reduce the resistance of fluid flow by expanding the effective pore size of microchannels. Hydraulic fracturing and acidizing and plugging removal have also been developed. Since the world’s first fracturing well was successfully fractured in the Hugoton field in Kansas in the United States in 1947, more than 1.5 million wells of hydraulic fracturing operations have been developed in more than 50 years.⁷ Ren⁸ found that the simultaneous hydraulic fracturing of two adjacent horizontal wells can enlarge the expansion area of hydraulic fractures to obtain a larger drainage area by taking two adjacent horizontal wells, namely, Yangping-1 and Yangping-2, in Longdong in China’s Changqing Oilfield. In 2012, China’s Shengli Oilfield implemented 58 wells of hydrochloric acid acidizing and plugging removal technology, with an efficiency of 87.5% and an effective period of 180 days; they also implemented 203 wells of hydrochloric acid + mud acid acidizing and plugging removal technology, with an efficiency of 91% and an effective period of 163 days. All of them have achieved a good injection effect.⁹ Gregory¹⁰ discovered following hydraulic fracturing,
large volumes of water containing very high concentrations of total dissolved solids (TDS) return to the surface. Wastewaters that contain high TDS levels are challenging and costly to treat. Guo\textsuperscript{11} reported that even high-concentration acid fluid cannot penetrate the core with barren natural fractures or calcium-filled fractures because of the ultralow permeability of the matrix in shale. The latter surface modification technology is performed to change the properties of a microchannel wall by injecting a certain number of modifiers into reservoir microchannels,\textsuperscript{12−14} thereby reducing the fluid flow resistance, mainly including the surfactant injection technology. Gogart\textsuperscript{15} proposed the use of surfactants and crude oil to form a miscible phase, thereby causing the oil retained after water flooding to migrate and consequently reducing the injection pressure. Foster\textsuperscript{16} found that reducing the oil−water interfacial tension to 0.001 mN/m can increase the capillary number to $10^{-2}$, thereby reducing the displacement pressure. Moradi\textsuperscript{17} showed that the effect of the concentration of active ions on wettability alteration is more significant than that on the decrease in oil−water interfacial tension.

The molecular film injection technology is a new technology that has been gradually developed in recent years. After a molecular deposition film is injected into a reservoir, anions and cations are electrostatically adsorbed to self-assemble a molecular deposition film on a rock surface so that the rock surface changes from an original hydrophilic form to a hydrophobic form.\textsuperscript{18−20} The water film originally adsorbed on the surface of a channel becomes thin, falls off, and flows away with the injected water. As a result, the water-blocking damage is eliminated, and the pore size is effectively expanded to reduce pressure and increase injection.\textsuperscript{21} Gao\textsuperscript{22} reported that molecular deposition films dissociate to form ions in an aqueous solution and avoid a “micelle” state in an increased concentration. Xiao\textsuperscript{23} found that polyelectrolyte molecular deposition films can decrease the adhesive force on a surface to modify the friction surface and reduce the friction force. Guo\textsuperscript{24} proposed that polyelectrolyte molecular deposition films have a lower friction force and a better antiwear property than those of a SiO$_2$ substrate under dry friction. The friction force of molecular deposition films is also lower than that of a substrate under water lubrication. Bai\textsuperscript{25} suggested that for quaternary ammonium-type cationic surfactants with similar hydrophobic tails, the ones with higher partial charges located on the H atoms on the methylene group should have superior wettability reversal performance.

This research was conducted to synthesize a washable polyelectrolyte molecular deposition film (PMDF) injection agent. Its basic properties, such as adsorption capacity, wettability, interfacial activity, and ζ-potential, were evaluated. The effects of PMDF and a commercially available Gemini surfactant on the depressurization and the stability of adsorption were compared through core displacement experiments. Then, the oil−water relative permeability curves and core nuclear magnetic resonance (NMR) experiments were used to visually characterize the distribution and aggregation of the fluid in the core. The efficiencies of porosity utility were quantitatively compared before and after the PMDF treatment.

2. RESULTS AND DISCUSSION

2.1. Characterization of PMDF. 2.1.1. IR Characterization. The chemical structure of PMDF was confirmed through IR spectroscopy (Figure 1). The broad peak at 3345 cm$^{-1}$ was due to the $\text{−NH}_2$ stretching band. The absorption peak at 2962 cm$^{-1}$ was a result of the stretching vibration absorption peak of $\text{−N}^+\text{−}$ and $\text{−CH}_2$. The absorption peak near 1660 cm$^{-1}$ was assigned to the stretching vibration of C=O in the amide group.\textsuperscript{26} The absorption peak near 1288 cm$^{-1}$ was caused by the stretching vibration of the C−N bond in the carbon−nitrogen five-membered heterocyclic ring, and the absorption peak near 653 cm$^{-1}$ was caused by the deformation vibration of the bond. The stretching vibration peak of the five-membered nitrogen heterocycle near 1448 cm$^{-1}$ confirmed the existence of the five-membered nitrogen heterocycle. This result indicated that dimethyl diallylammonium chloride (DMDAAC) and acrylamide (AM) reacted to form PMDF containing a five-membered nitrogen heterocycle.

2.1.2. 1H NMR Characterization. Figure 2 displays the 1H NMR spectra of PMDF. The chemical shift values at 1.81 ppm were attributed to the proton peaks of methylene $\text{−CH}_2$ in AM. The observed signal peak at 2.35 ppm was assigned to the proton peak of methine $\text{−CH}$ linked to the amide group in AM. The peak values at 3.25 and 3.15 ppm were due to the proton peaks of methyl $\text{−CH}_3$ linked to $\text{−N}^+$ in DMDAAC. At 3.91 and 3.90 ppm, the proton peaks of methylene $\text{−CH}_2$ were linked to $\text{−N}^+$ in DMDAAC. Hence, the structure of PMDF was consistent with the initial design based on the 1H NMR data.

2.2. Adsorption Capacity. 2.2.1. Standard Curve. Absorbance was measured on the basis of the known PMDF solution concentration (5−50 mg/L) using the UV−vis spectrophotometer at a wavelength of 590 nm. A standard curve was drawn with brine as the reference solution (Figure 3) and fitted the standard curve of PMDF in accordance with the Lambert−Beer law.

In Figure 3, its linear equation is $y = 0.02209x + 0.06753$, $R^2 = 0.9972$, which proves that the linear relationship between the concentration of the PMDF solution and the absorbance is good and has good fitting, so this method could be used to measure the concentration of PMDF. The PMDF solutions with a concentration higher than 50 mg/L were diluted in this range for measurement.

2.2.2. Static Adsorption. A PMDF solution with a mass concentration of 50−2000 mg/L was prepared and adsorbed on the sand for 24 h at 65 °C (Figure 4). The Langmuir and Freundlich models were commonly used to describe the adsorption isotherm. The adsorption isotherm data were also analyzed on the basis of the Langmuir and Freundlich models (Table 1).

The adsorption capacity of the PMDF solution increased with the concentration (Figure 4). However, the amount of
adsorption almost no longer increased when a certain concentration of the PMDF solution was reached, i.e., the equilibrium adsorption concentration. The adsorption equilibrium concentration of PMDF was 1500 mg/L.

Figure 4 shows the Langmuir and Freundlich plot of the adsorption of PMDF on the sand at 65 °C. Hence, the equilibrium data were accommodated well by the Langmuir model, with high correlation coefficients (Table 1). The maximum adsorption capacity at 65 °C obtained from the Langmuir model was 1629.38 μg/g. The derivation of the data indicated that the PMDF concentration increased, and the adsorption amount of PMDF on the sand increased simultaneously. This observation was also consistent with the experimental data in Figure 4. The trend in the change in the adsorption isotherms implied that the adsorption of PMDF on the sand was mainly the monolayer adsorption.

2.2.3. Dynamic Adsorption. The adsorption retention of the PMDF solution (1500 mg/L) in porous media and physical parameters of core are shown in Table 2. The concentration profile of the produced fluid is shown in Figure 5. It can be seen from Figure 5 that after the PMDF solution was injected, the concentration of PMDF in the produced fluid started to increase with a low rising rate, which indicated that PMDF was easy to be absorbed. When the injection volume reached about 6 pore volume (PV), the PMDF concentration in the produced fluid reached the maximum, which was similar to the PMDF concentration in the injection fluid, indicating that the adsorption of the PMDF solution in the porous medium at this time basically reached equilibrium. At this moment, the saturated adsorption capacity was 397.70 μg/g. After water flooding, the concentration of PMDF in the produced fluid continued to decrease until it was close to zero.
PMDF increased, its interfacial tension decreased and then gradually smoothened. When the mass concentration was greater than 1000 mg/L, the decrease became gentle. Although PMDF could reduce the interfacial tension of oil and water, the oil–water system was still a high interfacial tension system (8.16 mN/m). The interfacial tension of oil and water could be reduced to about 0.13 mN/m compared with that of DF-G. PMDF could not significantly reduce interfacial tension.

Although PMDF was not a surfactant, a certain adsorption and enrichment phenomenon would occur at the oil–water interface because of electrical effects. With the polar active components (such as colloid and asphaltene) in the crude oil on the interface, a small number of surface-active compounds were generated, and the composition of the interface changed, so the oil–water interfacial tension was reduced. Consequently, the residual oil saturation decreased, the permeability of the water phase near the wellbore improved, and the injection capacity enhanced.

### 2.3.2. Contact Angle
Wettability is significant since it determines fluid distribution in the reservoir and, thus affecting reservoir production and waterflood recovery. Figure 7 illustrates the contact angles between the core slice soaked in the PMDF solution and the brine. In the control experiment where brine was soaked, the contact angle was 22.32°, confirming that the core slice surface should be originally

![Figure 7. Contact angles of water and adsorption capacity in the core slice soaked in the PMDF solution.](Image 351x91 to 537x218)
water wet. After the core slice was soaked with the PMDF solution, the contact angle was 35.71°. The contact angles distinctly increased from 22.32 to 73.31° as the concentration of the PMDF solution increased. This result showed that PMDF could change the wettability of the core from hydrophilic wetting to neutral wetting. The change in wettability reduces the adhesion of the rock surface to water, thereby facilitating the flow of water in the pores.

The core slice was immersed in the PMDF solution for a long time so that the cationic groups in PMDF could be gradually adsorbed on the surface of the core slice through electrostatic attraction to form an adsorption layer with the hydrophobic group facing outward. As shown in Figure 7, the greater the concentration, the higher the amount of adsorption, and the larger the degree of change in the core slice surface to a weakly hydrophilic surface. However, as the concentration of the PMDF solution increased further, the adsorption tended to be saturated, the amount of adsorption was basically unchanged, and the contact angle tended to be stable.

2.4. ζ-Potential. Figure 8 shows the ζ-potential when the sand was dispersed in the PMDF solutions with different concentrations and the ζ-potential when PMDF was not detected after it was scoured with water. When the PMDF concentration was 0 mg/L, the ζ-potential was −16.23 mV, indicating that the sand itself was negatively charged. As the PMDF concentration increased, the ζ-potential on the surface of the sand increased rapidly from negative to positive and gradually reached a stable value of 51 mV. When the PMDF concentration was low, the PMDF molecules became preferentially adsorbed on the points with a higher charge density through electrostatic interaction. When the ζ-potential of the sand in the PMDF solution was greater than zero, the increase in the ζ-potential slowed down as the PMDF concentration increased. The main effect between the PMDF and sand was electrostatic interaction. When the electric charge in the solution was the same, the subsequent adsorption of PMDF on the surface of the sand decreased because of the repulsion of the electric charge, and the adsorption tended to be saturated.

When the sand dispersed in the PMDF solution was scoured with water, a part of the PMDF adsorbed on the surface of the sand was desorbed, thereby forming a new adsorption equilibrium. The ζ-potential was basically maintained at 38 mV. PMDF had a strong adsorption force on sand, was not easy to be desorbed, and had good stability of adsorption.

2.5. Depressurization and Increasing Injection. The change in the injection pressure during water flooding is shown in Figure 9 and Table 3. After the injection of PMDF, the injection pressure of the subsequent water flooding decreased more greatly compared with that after the injection of DF-G. After a long-term high-speed water flow, the stability of water flooding was stronger.

In Figure 9, during the starting of water flooding, the pressure initially increased to a maximum value and then decreased to the equilibrium value because a certain starting pressure must be overcome for low-permeability cores. A layer of boundary the fluid could not easily flow on the surface of the low-permeability core. The smaller the permeability of the core, the greater the resistance to overcome the movement of the fluid flow, and the greater the starting pressure gradient. As shown in Table 3, the initial flooding pressures of saturated water in core #1 and core #2 were 0.39 and 0.44 MPa, respectively. The equilibrium pressures during the subsequent water injection at a flow rate of 0.1 mL/min were 0.16 and 0.23 MPa, respectively. The depressurization rate of PMDF was 58.97%, and the depressurization rate of DF-G was 47.73%. After 30 PV of water was scoured at a flow rate of 0.1 mL/min were 0.16 and 0.23 MPa, respectively. The depressurization rate of PMDF was 58.97%, and the depressurization rate of DF-G was 47.73%. After 30 PV of water was scoured at a flow rate of 0.2 mL/min, the displacement pressures of PMDF and DF-G were 0.22 and 0.34 MPa, respectively. For the core treated with PMDF, the pressure only increased by 0.06 MPa, and the pressure drop rate was still as high as 43.59%. For the core treated with DF-G, the pressure drop rate was only 22.73%. The water flooding pressure of the core treated with PMDF increased under the scouring of high-speed water flow, but the increase was not large, and it remained at a relatively low injection pressure. This result showed that PMDF had better resistance to scouring after it was adsorbed on the rock. After PMDF was injected into the reservoir, even after the long-term water washout, it could still maintain a low injection pressure for a long time and had long-term effective properties.

After water flooding, the core is taken out and the contact angle of water on the injection end surface is measured. Similarly, after slug injection of PMDF solution and after subsequent water flooding, the core is taken out and the contact angle of water is measured again on the injection end surface. The contact angle of water on the injection end surface is measured.

![Image](https://dx.doi.org/10.1021/acsomega.0c04084)

Figure 9. Curve of the injection pressure of water flooding after PMDF and DF-G treatments.
the subsequent water flooding represents the remaining capacity of PMDF.

It can be seen from Figure 10 that the wettability of the core after water flooding is the same as that measured before the displacement experiment. The water contact angle is 19.12°, which proves that the core itself is strongly hydrophilic. At this time, after the water enters the core, due to the hydrophilic effect of the core, the water is tightly adsorbed on the pore wall, forming an immobile water film, which increases the flow resistance of the water, so the injection pressure is high. After slug injection of a PMDF solution, the contact angle of water is 70.44° at the injection ends, and the wettability of the core surface changes from strong hydrophobic to weak hydrophilic, which greatly reduces the flow resistance of water in the pores, thereby reducing the injection pressure. During the subsequent water flooding, the water flow continuously scoured the core, causing part of the PMDF to be desorbed, the core contact angle decreased to 58.32°, and the injection pressure also increased slightly.

2.6. Oil–Water Relative Permeability. As a fundamentally important parameter to study multiphase flow in porous media, relative permeability can characterize the relative transport capability of each fluid. Understanding the relative permeability of multiphase flow in porous media is crucial for the efficient development of water flooding reservoirs.

It can be seen from Figure 11 that the characteristics of the relative permeability curve of the core during water flooding are: the relative permeability of the oil phase drops rapidly, the water phase permeability curve is convex, and the irreducible water saturation and residual oil saturation are both high, so the two-phase flow zone is compressed. It can be seen from the variation trend of the two-phase flow curves that before the isotonic point, as the water saturation increases, the relative permeability of the oil phase drops sharply, indicating that the water phase in the core has a strong interference with the oil phase flow. The analysis suggests that the pore throat of the low-permeability core is very small. When fluid flows through the porous medium, a fluid adsorption and retention layer, that is, a boundary layer, forms on the surface of the porous medium. When the water enters the core, due to the hydrophilic effect of the core, the water is tightly adsorbed on the pore wall, forming a layer of an immobile water film, compressing the flow channel of the oil phase, thus greatly reducing the permeability of the oil phase. As the water saturation in the core gradually increases, the water phase occupies the main channel, and a small amount of oil phase is gradually dispersed into small oil droplets. When the small oil droplets move to the vicinity of the tiny throat, an additional resistance is generated due to resistance and deformation. At this time, the flow of oil and water is more difficult. Therefore, the relative permeability of the water phase increases more and more slowly, and the final value is also low.

When water flooding is performed after PMDF treatment, the characteristics of the relative permeability curve of the core are: the relative permeability of the oil phase drops rapidly but it is more gradual than the drop before treatment, and the relative permeability curve of the water phase is concave. The irreducible water saturation decreased from 35.923% to 23.303%, the residual oil saturation decreased from 29.264 to 19.136%, and the relative permeability of the water phase corresponding to the residual oil saturation increased from 15.454 to 28.908%. As the isotonic point moves to the left, the relative permeability corresponding to the isotonic point also increases. Analysis believes that the injection of PMDF can make it adsorb on the surface of the core, change the wettability of the core surface from hydrophilic to neutral wettability, and reduce the flow resistance of the boundary layer fluid. The fluid can overcome the force of surface molecules and participate in the flow with a small displacement pressure difference in the small pores. Therefore, after the PMDF is injected into the treatment, the oil and water are more likely to flow in the porous media.

2.7. Core NMR. The pore structure before and after the PMDF treatment was experimentally examined through NMR to further study the state of the fluid in the pores and the characteristics of the movable fluids. In Figure 12 and Table 4, the results indicated that the irreducible water saturation was

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**Table 3. Influence of the Scouring Rate on the Effect of Depressurization and Increasing Injection**

| samples | types of injection agents | water flooding pressure (MPa) | subsequent water flooding pressure (MPa) | depressurization rate (%) |
|---------|---------------------------|-----------------------------|------------------------------------------|---------------------------|
| #1      | PMDF                      | 0.39                        | 0.16, 0.22                               | 43.59                     |
| #2      | DF-G                      | 0.44                        | 0.23, 0.34                               | 22.73                     |

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**Figure 11. Oil–water relative permeability curves before and after PMDF treatment.**

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**Figure 10. Change of the core water contact angle under different displacement methods.**

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reduced from 90.70 to 72.57%, and the $T_2$ cutoff value was reduced from 12.33 to 1.75 ms. The proportion of porosity in the flowable part of the core and the water flooding swept volume increased, and more water was displaced in the core after PMDF injection.

In Figure 12A, the NMR porosity before the PMDF treatment was 6.88%, the NMR porosity after the displacement was 6.24%, the NMR porosity after the displacement was reduced by 0.64%, and the $T_2$ cutoff value was 12.33 ms. The irreducible water saturation of the core was as high as 90.70%, indicating that only 9.30% of the water in the pores was displaced. Our analysis revealed that this phenomenon was because the bound water in the reservoir included two parts: clay-bound water and capillary-bound water. Clay-bound water

| project                  | NMR porosity (%) | NMR irreducible water saturation (%) | $T_2$ cutoff value (ms) |
|--------------------------|------------------|--------------------------------------|-------------------------|
| before PMDF treatment    | saturated water  | 6.88                                 | 90.70                   | 12.33                   |
|                          | gas flooding     | 6.24                                 |                         |                         |
| after PMDF treatment     | saturated water  | 7.11                                 | 72.57                   | 1.75                    |
|                          | gas flooding     | 5.16                                 |                         |                         |

Figure 12. NMR porosity before (A) and after (B) PMDF treatment.

Figure 13. Histogram of the pore radius in the saturated and displacement states before and after the PMDF treatment.
is due to the adsorption of polar water molecules on the surface of clay particles to form a water film on the surface of the clay, while capillary-bound water is residual water trapped in the contact between a small capillary channel and the particles when the displacement pressure cannot overcome the resistance caused by the capillary force. Under natural conditions, bound water cannot flow freely. In Figure 12B, the NMR porosity after the PMDF treatment was 7.11%, and the NMR porosity after the displacement was 5.16%, i.e., a decrease of 1.95%. The core NMR analyzer is used to measure the signal of the fluid hydrogen nucleus (H) in the core pores. After the PMDF treatment, the swept volume of water flooding increased, and the proportion of porosity in the flowable part of the core increased from 6.88 to 7.11%. At the same time, the irreducible water saturation was reduced from 90.70 to 72.57%, and the $T_2$ cutoff value decreased from 12.33 to 1.75 ms. This result indicated that the movable fluid in the core increased, and more water molecules were easily displaced. When the core was initially saturated with water, a thick water film was adsorbed on the rock surface, thereby causing water-blocking damage in some pore throats. The water-blocking damage in the smaller throat was more serious. After the PMDF treatment, PMDF adsorbed on the rock surface, changed the wettability of the rock surface, stripped off the water film adsorbed on the rock surface, and released the water-blocking damage. After the treatment, the adhesion of the rock surface to water was reduced, and this condition was conducive to the flow of water in the pores. As such, a part of the bound water was in a flowing state. Therefore, when displacement occurred after water was saturated by the PMDF treatment, the pores that were not fully saturated with water became further saturated, the irreducible water saturation decreased, and the movable fluid increased.

$T_2$ can be approximately converted into the pore radius because fluids have different relaxation times when they flow in pores with different sizes. In this way, an online measurement technology for the NMR pore-radius distribution was adopted to quantitatively compare the efficiencies of porosity utility before and after PMDF treatment (Figure 13).

In Figure 13, the measurement results with the core saturated with water showed that pores with a radius of less than 0.1 $\mu$m accounted for 84.38%, of which less than 0.01 $\mu$m corresponded to 35.50%. The core had low porosity, small permeability, and small throats. Among them, the pores with small throats accounted for a large proportion of the entire core pores, so the water-blocking damage was more serious. It can be seen from Figure 13A that during nitrogen flooding, in the part with pore throats of less than 0.01 $\mu$m, a thick water film was attached to the rock surface, causing water-blocking damage in the throats. Therefore, the proportion of this part of NMR porosity in the pore-radius distribution did not change. As shown in Figure 13C,D, the proportion of porosity with a pore radius greater than 0.1 $\mu$m was significantly reduced, indicating that this part of the pore was the main movable fluid part, and the water in this part of the pore could be driven out under the displacement pressure of nitrogen. However, as shown in Figure 13B, the NMR porosity of the pores with a pore radius between 0.01 and 0.1 $\mu$m was increased. It is because that part of the water in large pores would be caught by the small pores when the displacement pressure cannot overcome the resistance caused by the capillary force. When the NMR test was conducted after the displacement pressure disappears, the residual water, which was shown as clay-bound water and capillary-bound water, condensed and returned to these pores, resulting in an increase in the proportion of the NMR porosity in some pores.

After the PMDF treatment, the NMR porosity of the core pore with a radius of less than 0.03 $\mu$m in saturated water accounted for different degrees of increase. Among them, the most obvious improvement occurs in those pore radius with 0.0–0.015 $\mu$m. When the external water was injected into the core, a layer of the water film was gradually attached to the surface of the reservoir rock, which reduced the pores radius of the core and even caused the water-blocking damage, and made it difficult for the subsequent injected water to enter the deep pore of the core. After the PMDF treatment, the water film attached to the rock surface peeled off, and the water-blocking damage was released. These conditions are conducive to the flow of water in the pores so that the pores are further filled with water. Therefore, the proportion of NMR porosity increased after the PMDF treatment.

In nitrogen flooding, the NMR porosity of the pores with a pore radius greater than 0.01 $\mu$m was significantly reduced, and only a small amount of residual water remained after the displacement because the pores with a pore radius greater than 0.01 $\mu$m were the main channels when the water in the partial pores was driven out. The molecular film was adsorbed on the rock surface, which changed the wettability of the rock surface, reduced the adhesion of the rock surface to water, and reduced the flow resistance of water in porous media. These conditions are conducive to increase the movable fluid in the core so that more water is easily displaced by nitrogen. However, the NMR porosity of the pores with a pore radius less than 0.01 $\mu$m has increased slightly. It is because the pore radius is small and the displacement pressure is less than its initial pressure, which causes the water in the pores of this part unable to flow. Therefore, after the PMDF treatment, the bound water of the pores with a pore radius between 0.01 and 0.1 $\mu$m was in a flowing state. The suitable range of PMDF according to pore-radius distribution within a low-permeability reservoir: the flowable partial pore required the throat radius greater than 0.01 $\mu$m.

### 3. CONCLUSIONS

1. In this study, AM and DMDAAC were used as monomers to synthesize a PMDF injection agent, whose structure was determined through IR and $^1$H NMR.

2. The performance evaluation results show that PMDF can change the hydrophilic wettability of the core surface to a neutral wettability and the negative $\zeta$-potential on the surface of the sand to a positive value. The core displacement experiment results reveal that the depressurization rate after the PMDF treatment is 58.97%. It is still as high as 43.59% under a high-speed water flow of 30 PV injection. It has good adsorption stability and ability to reduce pressure.

3. The oil–water relative permeability curves and core NMR experiments demonstrate that the PMDF treatment can reduce the irreducible water saturation, which indicated that the flowable part of the core increased and the swept volume was increased. The suitable range of PMDF according to pore-radius distribution within a low-permeability reservoir: the flowable partial pore required the throat radius greater than 0.01 $\mu$m.
4. EXPERIMENTAL SECTION

4.1. Materials. Acrylamide (AM), dimethyl diallyl ammonium chloride (DMDAAC), sodium hydrogen sulfite (NaHSO₃), ammonium persulfate ((NH₄)₂S₂O₈), and ethyl alcohol (C₂H₅OH) were purchased from Aladdin Chemical Reagent Company. They were analytical reagents and used as received. The commercially available Gemini surfactant DF-G was obtained from DongFeng Chemical Industry Co., Ltd., Shandong City, China. Deionized water was utilized in the synthesis and characterization experiments. A brine with 49 350 mg/L total salinity was used to prepare the experiments. The ionic composition is shown in Table 5.

Petrophysical properties of the core samples and sand (core powder) are shown in Figure 14.

4.2. Preparation and Characterization of PMDF. AM and DMDAAC were used as monomers. The initiators of the synthesis of PMDF were NaHSO₃ and (NH₄)₂S₂O₈. PMDF was synthesized as follows. First, AM and DMDAAC were mixed in deionized water at a molar ratio of 4:1 (monomer concentration of 26%). Second, the reaction vessel was placed in a water bath at a constant temperature of 60 °C and preheated. The pH of the mixed solution was adjusted to 7. Third, NaHSO₃ in deionized water and (NH₄)₂S₂O₈ in deionized water at a molar ratio of 1:1 were injected into the mixture (the amount of initiator = 0.4 wt %). The reaction vessel was heated in a water bath at 60 °C for 4 h. Fourth, the reaction product was precipitated (thrice) from C₂H₅OH and then dried in a drying oven at 50 °C for 12 h. The scheme of the synthesis route is shown in Figure 15.

The infrared (IR) spectra of KBr pellets were analyzed using a WQF-520 infrared spectrometer (Beijing Rayleigh Analytical Instrument Co., Ltd., Beijing City, China). PMDF was characterized through IR. ³¹H nuclear magnetic resonance (³¹H NMR) analysis was performed using a Bruker AC-E 200 NMR spectrometer (Bruker Daltonics Inc., Billerica City, Massachusetts, USA) with D₂O as a solvent.

4.3. Adsorption Capacity Test. Static adsorption: tests were performed with a UV-1800 ultraviolet−visible spectrophotometer (Beijing Ruili Analytical Instruments Co., Ltd., Beijing City, China). First, PMDF was diluted with brine into solutions with different concentrations. Second, the sand and the PMDF solution were stirred at a solid−liquid mass ratio of 1:5 to produce a uniform solution that was then added to an Erlenmeyer flask. Then, the solution was placed in a shaking water bath for 24 h at 65 °C. The supernatant liquid was used to determine the adsorption capacity. The static adsorption capacity was determined via the starch-cadmium iodide method³⁰,³¹ and calculated using eq 1

\[
\Gamma = \frac{V(C_0 - C_1)}{G}
\]  

where \(\Gamma\) is the amount of PMDF absorbed per unit weight of the sand (µg/g), \(V\) is the volume of the PMDF solution (mL), \(G\) is the mass of the sand (g), and \(C_0\) and \(C_1\) are the initial and liquid-phase concentrations of the PMDF solution (mg/L), respectively.

Dynamic adsorption: the core was placed in the core holder and injected with 1500 mg/L PMDF solution at 65 °C until the PMDF concentration in the produced fluid was close to the injected concentration. Then, water flooding was performed until the PMDF concentration in the produced fluid was equal to or close to zero. The adsorption retention can be calculated according to eq 2

\[
R = \frac{C_0 V_0 - \sum_{i=1}^{n} C_i V_i}{W}
\]

where \(R\) is the adsorption retention of PMDF (mg/g), \(W\) is the dry weight of the core (g), \(C_0\) and \(C_i\) are the injection and outflow concentrations of the PMDF solution (mg/mL), respectively, and \(V_0\) and \(V_i\) are the injection and outflow volumes of the PMDF solution (mL), respectively.

4.4. Interfacial Tension and Contact Angle Test. The static interfacial tension between crude oil, PMDF, and DF-G was directly measured using a Germany KRUSS DSA30S interface parameter measurement apparatus (Shanghai Kruss Scientific Instruments Co., Ltd., Shanghai City, China). PMDF was diluted with brine into solutions with different water types.

Table 5. Ionic Composition of the Brine

| cationic (mg/L) | anionic (mg/L) | pH | total salinity (mg/L) | water type |
|----------------|---------------|----|----------------------|------------|
| Na⁺ + K⁺       | Cl⁻           |    |                      |            |
| 16741           | 29328         |    | 6.0                  | 49 350     |
| Ca²⁺           | SO₄²⁻         |    |                      | CaCl₂      |
| 1768           | 471           |    |                      |            |
| Mg²⁺           | HCO₃⁻         |    |                      |            |
| 387            | 658           |    |                      |            |

Figure 14. XRD pattern of core and sand.

Figure 15. Synthesis route of PMDF.
concentrations. The interfacial tension was determined at 65 °C. All measurements were repeated at least thrice until the values were reproducible.

Contact angel tests were carried out using the same apparatus. PMDF was diluted with brine into solutions with different concentrations, and then a core slice (25 mm × 25 mm × 5 mm) soaked in a PMDF solution for 24 h at 65 °C. The contact angle of water measurements was analyzed on the surface of the core slice after PMDF treatment. The supernatant liquid after soaking was used to determine the adsorption capacity. Refer to Section 4.3 for the determination method of adsorption capacity.

4.5. ζ-Potential Test. The tests were performed with a Zeta PALS 190 Plus potential analyzer (Brookhaven Instruments Corporation, Austin City, Texas). First, the sand and different concentrations of the PMDF solutions were stirred at a solid–liquid mass ratio of 1:5 to produce a uniform solution that was then added to an Erlenmeyer flask and placed in a shaking water bath for 24 h at 65 °C. Afterward, the supernatant liquid was utilized to determine the ζ-potential. The sand was scoured with water until PMDF was no longer present in the supernatant. The ζ-potential was measured again. Each sample was measured at least three times, and the test results were averaged.

4.6. Evaluation of the Effects of Depressurization and Increasing Injection. The basic physical parameters of the core are presented in Table 6. The designed core confining pressure was 10 MPa, and the experimental temperature was 65 °C. The experiments were conducted as follows: first, the core was vacuum dried at 100 °C for 24 h. Brine was injected into the core at a constant rate of 0.1 mL/min. The displacement pressure was recorded until the pressure generated through the core was stable. Second, oil flooding was used to displace the movable fluid in the core to establish irreducible water saturation. A low flow rate (0.1 mL/min) was used for oil flooding and the displacement speed was gradually increased until no water was produced. Then, after displacement of 10 times the pore volume with the oil, the permeability of the oil phase in the state of bound water was measured. At last, the water flooding experiment was performed at a displacement speed of 0.1 mL/min. The water breakthrough time, the cumulative oil production when the water breakthrough, the cumulative fluid production, and the displacement speed and the displacement pressure difference between the two ends of the rock were recorded accurately. When the water content reached 99.95% or 30 times the pore volume after water flooding, the water permeability under the residual oil was measured and the experiment ended.

The experiment is a comparative experiment of the relative permeability of the core before and after PMDF treatment. To reduce or eliminate the influence of lithology on the relative permeability of oil and water, after completing the experiment of the relative permeability curve of oil–water before PMDF treatment, the core used in the experiment was distilled with toluene–ethanol system, washed, and dried. Then, the relative permeability experiment of core after PMDF treatment was carried out.

PMDF treatment steps: after the core was saturated with brine, 1 PV of PMDF solution with a concentration of 1500 mg/L was injected at a flow rate of 0.1 mL/min and subjected to core aging for 24 h.

4.8. Core NMR Analysis. The object of NMR technology, which is an indirect measurement technology, is the hydrogen and the stability of scouring resistance. The schematic of the experimental device is shown in Figure 16.

### Table 6. Basic Physical Parameters of Low-Permeability Cores

| samples | length (cm) | diameter (cm) | porosity (%) | gas permeability (10⁻¹³ μm²) |
|---------|-------------|---------------|--------------|-----------------------------|
| #1      | 4.996       | 2.475         | 9.56         | 2.37                        |
| #2      | 5.018       | 2.501         | 7.32         | 1.78                        |

4.7. Measurement of Oil–Water Relative Permeability. According to the unsteady-state method in the Chinese national standard GB/T 28912–2012, the core oil–water relative permeability curves before and after PMDF treatment were measured. The basic physical parameters of the core are presented in Table 7. The designed core confining pressure was 10 MPa, and the experimental temperature was 65 °C. The experiments were conducted as follows: first, the core was vacuum dried at 100 °C for 24 h. Brine was injected into the core at a constant rate of 0.1 mL/min. The displacement pressure was recorded until the pressure generated through the core was stable. Second, oil flooding was used to displace the movable fluid in the core to establish irreducible water saturation. A low flow rate (0.1 mL/min) was used for oil flooding and the displacement speed was gradually increased until no water was produced. Then, after displacement of 10 times the pore volume with the oil, the permeability of the oil phase in the state of bound water was measured. At last, the water flooding experiment was performed at a displacement speed of 0.1 mL/min. The water breakthrough time, the cumulative oil production when the water breakthrough, the cumulative fluid production, and the displacement speed and the displacement pressure difference between the two ends of the rock were recorded accurately. When the water content reached 99.95% or 30 times the pore volume after water flooding, the water permeability under the residual oil was measured and the experiment ended.

The experiment is a comparative experiment of the relative permeability of the core before and after PMDF treatment. To reduce or eliminate the influence of lithology on the relative permeability of oil and water, after completing the experiment of the relative permeability curve of oil–water before PMDF treatment, the core used in the experiment was distilled with toluene–ethanol system, washed, and dried. Then, the relative permeability experiment of core after PMDF treatment was carried out.

PMDF treatment steps: after the core was saturated with brine, 1 PV of PMDF solution with a concentration of 1500 mg/L was injected at a flow rate of 0.1 mL/min and subjected to core aging for 24 h.

4.8. Core NMR Analysis. The object of NMR technology, which is an indirect measurement technology, is the hydrogen

![Figure 16. Schematic of the experimental device.](https://dx.doi.org/10.1021/acsomega.0c04084)
nucleus (H) in the pore fluid of the core. The collected image signal data reflect the distribution and aggregation of the fluid in the core and the interface effect between the fluid and the surrounding rock surface. Currently, the most widely used techniques are NMR relaxation curves and NMR imaging. In the petroleum industry, an NMR spectrometer is usually used to measure $T_2$ relaxation time. When a pore contains only a single liquid, the $T_2$ value is proportional to the pore size, so the $T_2$ value is commonly utilized to reflect the size of the pore in the core. The longer the $T_2$ relaxation time, the larger the pore diameter, whereas the shorter the $T_2$ relaxation time, the smaller the pore diameter. A limit exists between the movable fluid and the bound fluid, and this boundary is defined as the $T_2$ cutoff value of the movable fluid on the $T_2$ spectrum. The fluid on the $T_2$ spectrum that is greater than the $T_2$ cutoff value is movable fluid; otherwise, it is a bound fluid. That is, the size of the $T_2$ cutoff value of the movable fluid is related to the pore size of a reservoir. The $T_2$ cutoff value of movable fluid is calibrated through the following. The $T_2$ cumulative curves of the $T_2$ spectrum are prepared before and after centrifugation, and a straight line parallel to the $x$-axis is made from the maximum value of the $T_2$ cumulative curve after centrifugation, and the $T_2$ cumulative curve is intersected before centrifugation. The vertical line of the $x$-axis drawn from the intersection point intersects the $x$-axis, and the relaxation time corresponding to the intersection point is the $T_2$ cutoff value of the movable fluid.

In this study, the experiments were conducted as follows. The designed core confining pressure was 10 MPa, and the experimental temperature was 65 °C. The core was vacuum dried for 24 h to eliminate the effect of bound water in the core on the NMR response. First, the core was initially saturated with brine: the brine was injected at a flow rate of 0.1 mL/min. After about 24 h, it was regarded as saturated. Second, nitrogen was used to displace the movable fluid in the core to establish irreducible water saturation until water was no longer flowing out of the outlet end of the core holder for about 1 h. Third, 1 pore volume (PV) of the PMDF solution with a concentration of 1500 mg/L was injected at a flow rate of 0.1 mL/min and subjected to core aging for 24 h. Then, the saturated brine was injected at a flow rate of 0.1 mL/min until the displacement pressure was stable. Finally, the displacement with nitrogen was repeated until water no longer flowed out at the outlet end of the core holder for about 1 h. After each step of the experiment, an AniMR-150 full-diameter core NMR imaging analysis system (Shanghai Niumag Electronic Technology Co., Ltd., Shanghai City, China) was used for measurement once. The basic physical parameters of the core are presented in Table 8.

| samples | length (cm) | diameter (cm) | gas permeability ($10^{-7}$ μm$^2$) |
|---------|------------|---------------|-----------------------------------|
| #4      | 5.024      | 2.502         | 2.30                               |

**AUTHOR INFORMATION**

**Corresponding Author**
Nanjun Lai — School of Chemistry and Chemical Engineering and Oil and Gas Field Applied Chemistry Key Laboratory of Sichuan Province, Southwest Petroleum University, Chengdu, Sichuan 610500, China; orcid.org/0000-0001-7881-028X; Phone: +86 13094484238; Email: lainanjun@126.com

**Authors**
Xintong Nie — School of Chemistry and Chemical Engineering and Oil and Gas Field Applied Chemistry Key Laboratory of Sichuan Province, Southwest Petroleum University, Chengdu, Sichuan 610500, China; orcid.org/0000-0002-6036-2201
Xu Zheng — Tianjin Branch of China National Offshore Oil Co., Ltd., Tianjin 300459, China
Wensen Zhao — State Key Lab Offshore Oil Exploit, Beijing 100027, China
Xubin Zhao — CNPC Xinjiang Oilfield Company, Karamay 834000, China
Yong Wang — CNPC Xinjiang Oilfield Company, Karamay 834000, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04084

**Notes**
The authors declare no competing financial interest.

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