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Abstract:

In this study, four relative permeability modifiers (RPMs) with distinct molecular structures—partially hydrolyzed polyacrylamide (HPAM), cationic RPM (RPM-I), hydrophobically associating RPM (RPM-II), and cationic hydrophobically associating RPM (RPM-III)—were synthesized using acrylamide, acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, cationic monomers and hydrophobically associating

monomers as feedstocks. Their structures were verified to match the designed configurations via FT-IR and ^1H NMR. Combining macroscopic core flooding evaluation with microscopic characterizations including hydrodynamic size measurement, desorption resistance assay and cryo-SEM, this study systematically elucidates how molecular structures affect injectivity and oil stabilization & water control performance.

The results demonstrate that Cationic groups anchor polymer chains onto pore walls via electrostatic interactions: anchored chains extend in water flow to obstruct aqueous seepage, and contract in oil flow to release flow paths. However, excessive surface chain density restricts conformational space, hindering full opening of oil flow paths. Hydrophobically associating groups strengthen intermolecular interactions and reduce wall adsorption, lowering surface chain density to enable sufficient chain contraction. Nevertheless, free chains tend to form “molecular clusters” that migrate to pore constrictions and cause plugging. RPM-III functionalized with both groups delivers optimal overall performance ($\lambda=0.26$, $N_W=68.72\%$, $N_O=14.48\%$), integrating superior injectivity, selective water control and long-term stability. Its injectivity greatly outperforms RPM-I ($\lambda=3.82$), and its efficacy and durability markedly surpass RPM-II ($N_W=46.61\%$, $N_O=29.52\%$). This study clarifies the synergistic regulation mechanism of the two functional groups, providing experimental evidence for molecular design and performance optimization of RPM systems.

Keywords: polymers; relative permeability modifiers; oil stabilization and water control; hydrophobically associating groups; cationic groups

Introduction

With the continuous exploitation of mature oilfields worldwide, the high water cut issue in produced fluids has become increasingly prominent. This not only significantly impairs the economic benefits of oilfield development ^[1], but also readily induces problems such as pipeline scaling and corrosion.

To address the high water cut challenge, oilfield practitioners have developed two primary categories of water control technologies: mechanical water control and chemical water control ^[2]. Mechanical water control ^[3-5] reduces water production by deploying downhole tools like packers in production wellbores to isolate water-producing intervals. Chemical water control ^[6-10], by contrast, achieves water-phase plugging mainly relying on chemical plugging agents including polymers ^[11], gels ^[12],

resins and cement ^[13].

However, as reservoir development advances, the oil-water relationship in the formation grows increasingly intricate, and the coexistence of oil and water phases has become widespread ^[14-16]. As a result, traditional mechanical water control methods and conventional chemical plugging agents can barely realize precise and efficient water control. Accordingly, relative permeability modifiers (RPMs) with selective water control performance have re-emerged in the research spotlight. Featuring the core property of disproportionately reducing oil and water phase permeabilities, they provide a novel technical pathway for solving the high water cut problem ^[17].

Relative permeability modifiers (RPMs) were first proposed by Sandiford in 1964 ^[18], and their pioneering application in water shutoff treatments was reported by White et al. in 1973 ^[19]. Since then, extensive research efforts have been dedicated to RPMs by scholars worldwide, yielding fruitful outcomes and giving rise to a diverse spectrum of RPM systems. The mainstream categories include cationic ^[20-22], anionic ^[23-25], hydrophobically associating ^[26-28], nonionic ^[29] and zwitterionic ^[30] polyacrylamides and their derivatives, as well as plant gums ^[31] and other systems.

Building on a large body of experimental investigations, researchers have summarized and established multiple action mechanisms and theoretical models, namely the wall effect ^[32-34], swelling-shrinkage effect ^[35-37], adsorption-entanglement effect ^[38-39], oil-water diversion theory ^[40], and gravity effect ^[41]. These findings have laid a more robust theoretical foundation for the subsequent molecular design and field application of RPMs.

Based on the aforementioned theoretical advances and our research group's established work on oilfield polymers, four polymers were synthesized using a subset or the full set of acrylamide, acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), cationic monomers and hydrophobically associating monomers as feedstocks, namely partially hydrolyzed polyacrylamide (HPAM), cationic relative permeability modifier (RPM-I), hydrophobically associating relative permeability modifier (RPM-II), and cationic hydrophobically associating relative permeability modifier (RPM-III). Using these four polymers as research subjects, the effects of the two types of functional groups on the injectivity of RPMs were investigated, and the underlying mechanisms were further elucidated via a series of characterization approaches including hydrodynamic size measurement, adsorption performance evaluation and cryo-SEM scanning.

In addition, by analyzing the impacts of the four polymers on oil/water phase permeability in cores, the influence law of the two functional groups on the oil stabilization and water control performance as well as the long-term water control effect of RPMs was revealed. Furthermore, the oil stabilization and water control performance of the RPMs was further validated through simulation of simultaneous oil-water seepage in the same reservoir layer.

1 Experimental Section

1.1 Experimental Materials and Apparatus

Experimental materials: Sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride hexahydrate (MgCl₂·6H₂O), sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃), sodium sulfate (Na₂SO₄), ammonium persulfate ((NH₄)₂S₂O₈), sodium sulfite (Na₂SO₃), sodium carbonate (Na₂CO₃), starch and cadmium iodide (all analytical grade) were purchased from Chengdu Kelong Chemical Co., Ltd. Quartz sand (60–80 mesh) was supplied by Chengdu Changyu Quartz Sand Factory. Sandstone cores (specific parameters are listed in Table 1) were provided by Southwest Petroleum University. Simulated crude oil (density: 0.726 g/cm³, viscosity at 70 °C: 0.620 mPa·s) was obtained from an oilfield in Xinjiang. Simulated brine (composition detailed in Table 2) was prepared with reference to the water quality of an oilfield in Xinjiang. Acrylamide (AM), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), sodium acrylate (NaAA), cationic monomer A and hydrophobically associating monomer B (all industrial grade) were provided by Sichuan Guangya Polymer Chemical Co., Ltd. The structural parameters of each relative permeability modifier (RPM) are summarized in Table 3.).

Table 1 Core parameters

Core length	Permeability	Porosity
10cm	180-220mD	35-37%

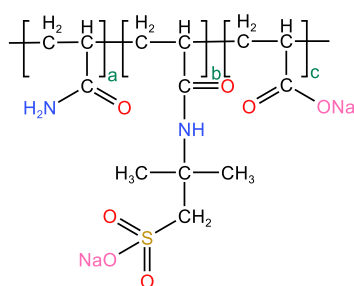
Table 2 Composition of simulated formation brine

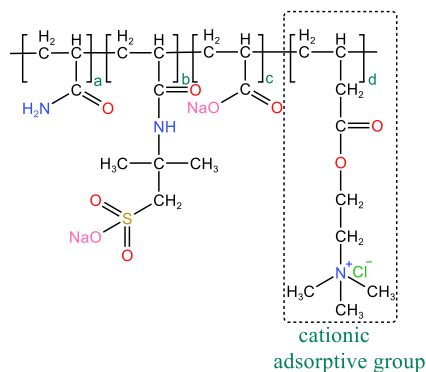
Ion concentration / $\text{mg}\cdot\text{L}^{-1}$							Total dissolved solids/ $\text{mg}\cdot\text{L}^{-1}$
$\text{K}^+ + \text{Na}^+$	Ca^{2+}	Mg^{2+}	Cl^-	CO_3^{2-}	HCO_3^-	SO_4^{2-}	
8622.07	21.41	6.11	11,333.50	185.72	3169.88	35.66	23,374.35

Table 3 Structural information of relative permeability modifiers

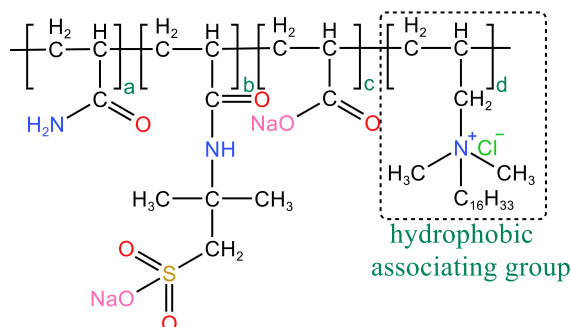
RPMs	Base monomer composition			Cationic group content ($\text{wt}\%$)	Hydrophobically associating group content ($\text{wt}\%$)	Viscosity-average molecular weight ($\times 10^4$ g/mol)	Applied concentration (mg/L)
	Acrylamide ($\text{wt}\%$)	Acrylic acid ($\text{wt}\%$)	AMPS ($\text{wt}\%$)				
HPAM	53.33	26.67	20	0	0	504	850
RPM-I	53.33	26.67	20	1.5	0	577	800
RPM-II	53.33	26.67	20	0	5	520	800
RPM-III	53.33	26.67	20	1.5	5	460	920

Table Notes: AMPS is the abbreviation for 2-acrylamido-2-methylpropanesulfonic acid. The base monomers (acrylamide, acrylic acid and AMPS) account for 30 wt% of the total mass of the aqueous reaction solution. The cationic group is methacryloyloxyethyl trimethyl ammonium chloride, and the hydrophobically associating monomer is hexadecyldimethylallylammonium chloride. Their contents are given as mass percentages relative to the total mass of base monomers in the feeding formulation.

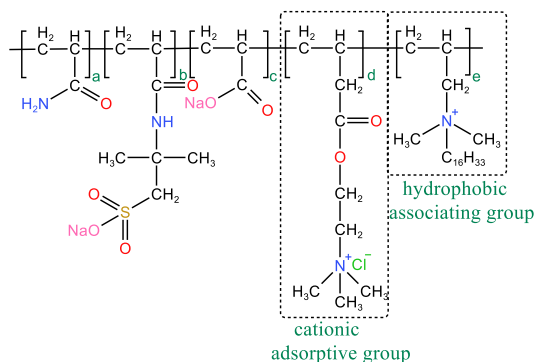
**(a) HPAM molecular structure**



(b) RPM-I molecular structure



(c) RPM-II molecular structure



(d) RPM-III molecular structure

Figure 1 Molecular structures of the relative permeability modifiers

Experimental apparatus: - Electric digital display stirrer, Model S212, Shanghai Shensheng Technology Co., Ltd. Capillary physical model ($\Phi 0.58 \text{ mm} \times 100 \text{ mm}$), Jiangsu Baoying Zhejiang Trading Business Department. WFUV-3802 UV-Vis spectrophotometer, UNICO (Shanghai) Instrument Co., Ltd. Core flooding apparatus, Southwest Petroleum University. Dynamic light scattering (DLS) instrument, Malvern Instruments Ltd., United Kingdom. Fourier transform infrared spectrometer (FT-IR), Thermo Scientific Nicolet iS20, United States. Liquid-state nuclear magnetic resonance spectrometer (NMR), Bruker 400 MHz, Germany.

1.2 Experimental Methods

1.2.1 Preparation of Relative Permeability Modifiers

Four relative permeability modifiers (RPMs) were synthesized via aqueous free radical polymerization in this work.

The detailed preparation procedure is as follows: ① Acrylic acid (AA) was added to a fixed volume of deionized water according to the predesigned formulation. NaOH solution was added dropwise under a low-temperature water bath for neutralization to prepare a sodium acrylate solution. ② Acrylamide (AM) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) were sequentially added. After complete dissolution under stirring, the pH of the system was adjusted to 7.0 using NaOH and aqueous acrylic acid solutions. ③ The cationic group (methacryloyloxyethyl trimethyl ammonium chloride) and the hydrophobically associating monomer (hexadecyldimethylallylammonium chloride) were introduced and stirred until fully dissolved to form a homogeneous monomer solution. ④ Different dosages of sodium formate were added as a chain transfer agent to regulate the molecular weight of the target polymers. ⑤ The reaction solution was heated to 40 °C, and the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ – Na_2SO_3 redox initiator system was added. The reactor was then sealed for 4 h of adiabatic polymerization. ⑥ After the polymerization was completed, the resulting polymer colloid was cut into small pieces and washed repeatedly with anhydrous ethanol to remove unreacted monomers and residual impurities. ⑦ The purified product was dried via forced air drying at 95 °C for 2 h, followed by crushing and grinding to obtain solid powder of the relative permeability modifiers.

1.2.2 Structural Characterization of Relative Permeability Modifiers

(1) FT-IR Spectroscopy

Fourier transform infrared (FT-IR) structural characterization was performed using the standard KBr pellet method. The purified RPM polymer powder was thoroughly ground and homogenized with potassium bromide (KBr) at a mass ratio of 1:200 in a mortar. The mixture was compressed into a pellet using a pellet press, followed by FT-IR spectrum collection.

(2) ^1H NMR Spectroscopy

The ^1H NMR spectra of the as-synthesized RPMs were acquired on an AVANCE III 400 nuclear magnetic resonance spectrometer at 20 °C, with deuterium oxide (D_2O)

serving as the testing solvent.

1.2.3 Injectivity and Effluent Concentration Characteristics of Relative Permeability Modifiers

1.2.3.1 Injectivity

Effective injection into target water-control reservoirs is critical for RPM to exert its relative permeability regulation function. The injection selectivity of RPM can be qualitatively assessed via injection pressure gradient profiles. For quantitative evaluation, the injection pressure gradient growth rate λ is proposed, based on which the injection performance is divided into four grades (see Table 4).

The experimental procedures are as follows: ① The injection pressure gradient (P_1) was recorded after injecting 1 pore volume (PV) of RPM solution; ② The injection pressure gradient (P_2) was recorded after injecting 10 PV of RPM solution; ③ The injection pressure gradient growth rate (λ) was adopted as the evaluation index for injectivity, where a higher λ corresponds to poorer injection performance. The calculation formula of λ is given in Equation (1).

$$\lambda = \frac{P_2 - P_1}{P_1} \quad (1)$$

where: λ is the growth rate, %; P is the polymer injection pressure gradient (P_1 : injection pressure gradient at 1 PV injection; P_2 : injection pressure gradient at 10 PV injection), $\text{MPa} \cdot \text{m}^{-1}$.

Table 4 Classification of injection performance

Injection performance grade	Grade I (Excellent)	Grade II (Good)	Grade III (Fair)	Grade IV (Poor)
Growth rate (λ) / %	0~0.5	0.5~1.0	1.0~1.5	> 1.5

1.2.3.2 Concentration Determination of Relative Permeability Modifiers in Effluent

The flow of RPMs in porous media is governed by multiple factors including electrostatic interactions. These factors collectively determine the adsorption, retention and flow characteristics of RPMs in porous media, and are critical for in-depth elucidation of the working mechanism of RPMs under actual reservoir conditions.

The experimental procedures are as follows: ① Artificial cores with a permeability of approximately 200 mD were saturated with simulated brine at a

constant temperature of 70 °C, and the core permeability and pore volume were measured; ② RPM solution with a kinematic viscosity of approximately 5 mm²/s was prepared and injected into the brine-saturated cores at a flow rate of 0.4 mL/min; ③ Effluent samples were collected at the core outlet at 1 PV intervals, and the polymer concentration C_i was determined using the starch-cadmium iodide method. The polymer loss and concentration retention rate in the core are given in Equations (2) and (3):

$$\Gamma_d = C_0 \sum_{i=0}^n V_i - \sum_{i=0}^n V_i C_i \quad (2)$$

$$\theta = \frac{C_i}{C_0} \times 100\% \quad (3)$$

Where: Γ_d is the polymer loss amount, µg/g; C_0 is the initial polymer concentration, mg/L; C_i is the polymer concentration in effluent at a specific time interval, mg/L; V_i is the effluent volume at the corresponding time interval, mL; θ is the concentration retention rate, %.

1.2.4 Hydrodynamic Size Measurement

Dynamic light scattering (DLS) was employed in this experiment. The particle size and size distribution characteristics of the samples were accurately determined by detecting the Brownian motion of particles and fitting the raw experimental data with relevant theoretical models. All measurements were performed at a constant temperature of 25 °C to eliminate the interference of temperature fluctuations on particle diffusion behavior.

The experimental procedures are listed as follows: ① Vessel pretreatment, medium purification and instrument calibration were sequentially completed prior to testing. ② The DLS instrument was switched on simultaneously and preheated for 30 min to complete calibration and zero adjustment. ③ Aqueous solutions of relative permeability modifiers (RPMs) with a mass concentration of 100 mg/L were prepared as the test systems. ④ An appropriate volume of the test solution was used to rinse the cuvette, followed by slow sample injection to avoid bubble entrainment. ⑤ The sample cell was placed in the instrument for thermal equilibrium. Once the system stabilized, test parameters were set and signal acquisition was launched. Each sample was measured in triplicate. ⑥ Upon completion of the test, the raw data were saved and processed for analysis using corresponding algorithms.

1.2.5 Desorption Resistance Test

The desorption resistance performance of relative permeability modifiers (RPMs)

on quartz sand surfaces was tested via the immersion method.

The specific experimental procedures are as follows: ① Place 60-80 mesh quartz sand and RPM solution in stoppered reagent bottles at a mass ratio of 1:4. Seal the bottles and immerse them in an oven at 70 °C for 48 h under constant temperature, to allow sufficient contact between the RPM and quartz sand and reach adsorption equilibrium. ② After adsorption is completed, decant most of the remaining RPM solution in the reagent bottle and accurately weigh it, recorded as m_1 . Combined with the total mass of the initially added RPM solution m_0 the total mass of the adsorbed phase on quartz sand surfaces and the residual RPM in the bottle m_2 is calculated by $m_2 = m_0 - m_1$. ③ Add an appropriate amount of pure water into the reagent bottle with retained quartz sand. Seal the bottle and place it on a constant-temperature shaker at 70 °C for reciprocating oscillation for 4 h to carry out the RPM desorption resistance test. ④ After oscillation, pipette the supernatant test solution and collect the supernatant clear liquid via high-speed centrifugation. The polymer concentrations of the test solutions after adsorption equilibrium and after water washing and elution are determined respectively by the starch-cadmium iodide method. ⑤ Based on the measured concentration data, analyze and evaluate the desorption resistance performance of the RPM on quartz sand surfaces. The calculation formulas for adsorption amount are shown in Equations (4)-(6):

$$\Gamma = \frac{V_0(C_0 - C_e)}{m} \quad (4)$$

$$\Gamma_d = \frac{(C_r V_r - C_e V_e)}{m} \quad (5)$$

$$\Gamma_r = \Gamma - \Gamma_d \quad (6)$$

Where Γ , Γ_d and Γ_r are the adsorption amount, desorption amount and residual adsorption amount of the polymer on quartz sand surfaces, respectively ($\mu\text{g/g}$). C_0 , C_e and C_r are the initial polymer concentration before adsorption, the concentration after adsorption and the concentration after desorption in the stoppered bottle, respectively (mg/L). V_0 , V_e and V_r are the volume of solution before adsorption, the volume of residual solution in the bottle before desorption and the volume of solution in the bottle after desorption, respectively (mL). m is the mass of quartz sand particles (g).

1.2.6 Cryo-SEM Scanning of RPM Adsorption Layers

To investigate the selective adsorption properties and micromorphological differences of four types of relative permeability modifiers (RPMs) on the inner wall

of capillaries, this study employs scanning electron microscopy (SEM) for microstructure characterization. SEM can effectively identify the interfacial boundary and morphological features between the capillary wall substrate and the polymer adsorption layer, providing microscopic evidence for revealing the differences in adsorption performance and action mechanisms of polymer-based RPMs with different molecular structures.

The specific experimental procedures are as follows: ① Fill the capillaries with relative permeability modifier (RPM) solution at a mass concentration of 0.1%, and conduct isothermal adsorption at 70 °C for 24 h to achieve saturated adsorption. ② After adsorption, continuously flush the capillaries with simulated brine at a flow rate of 10 mL/min for 8 h to remove free RPM molecules and stabilize the adsorption layer on the capillary wall. ③ Prepare flat cross-sectional samples from the treated capillaries via cryo-fracture in liquid nitrogen, and store them at low temperature. ④ Select intact cross-sectional samples, fix them on a sample stage with conductive adhesive, and perform gold sputtering pretreatment to improve imaging quality. ⑤ Place the samples in the SEM sample chamber. After the chamber reaches vacuum condition, conduct microscopic scanning on the capillary cross-sections to observe and acquire the microstructural and morphological characteristics of the capillary wall and the RPM adsorption layer.

1.2.7 Oil Stabilization and Water Control Tests

1.2.7.1 Aqueous and Oil Phase Plugging Rate Test and Long-Term Performance Test

Artificial cores with a permeability of approximately 200 mD and a porosity of approximately 35% were adopted. Under a constant temperature of 70 °C, a relative permeability modifier (RPM) solution with a kinematic viscosity of 5 mm²/s was injected into the core at a constant flow rate of 0.4 mL/min. The relative permeabilities of the aqueous phase and oil phase in the core before and after RPM solution treatment were measured. The schematic diagram of the experiment is shown in Figure 2:

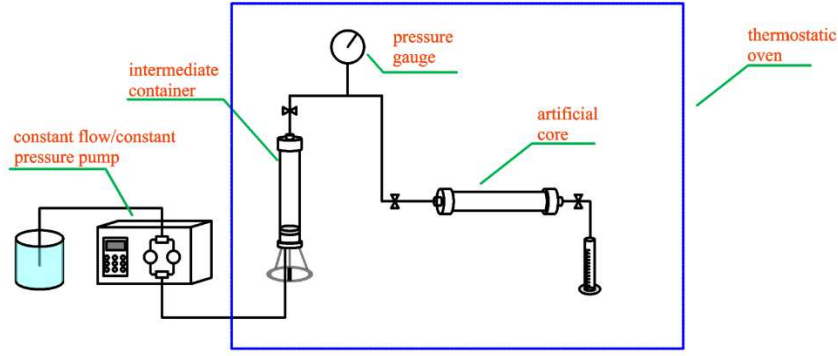


Figure 2 Schematic diagram of the core flooding experimental setup

The experimental procedures are as follows: ① Saturate the core with brine, then measure its pore volume (PV) and initial water phase permeability (K_{w0}). ② Inject oil in the forward direction until the pressure stabilizes, and measure the oil phase permeability (K_{o1}). ③ Inject water in the forward direction until the pressure stabilizes, and measure the water phase permeability (K_{w1}). ④ Inject 10 PV of RPM solution into the core in the reverse direction at a constant flow rate of 0.4 mL/min. ⑤ Inject water in the forward direction until the pressure stabilizes, and measure the water phase permeability (K_{w2}). ⑥ Inject oil in the forward direction until the pressure stabilizes, and measure the oil phase permeability (K_{o2}).

The water-oil seepage regulation capacity of the RPM is evaluated by the plugging rate (N), as shown in Equations (7)-(8):

$$N_W = \frac{K_{W1} - K_{W2}}{K_{W1}} \times 100\% \quad (7)$$

$$N_O = \frac{K_{O1} - K_{O2}}{K_{O1}} \times 100\% \quad (8)$$

where: N_W is the water plugging rate, %; N_O is the oil plugging rate, %.

On this basis, the long-term performance test was conducted: ⑦ Continuously inject 60 PV of simulated brine into the treated core, and measure the water phase permeability (K_{w3}) after the injection is completed. ⑧ Inject oil in the forward direction until the pressure stabilizes, and measure the oil phase permeability (K_{o3}).

The flow rate for RPM injection flooding is 0.4 mL/min, and the flow rate for all other flooding steps is 1.25 mL/min.

1.2.7.2 Oil-Water Isobaric Co-Seepage Test

The water/oil phase permeability tests before and after RPM treatment in cores are generally performed under single-phase flooding conditions, i.e., water phase

displacing oil phase or oil phase displacing water phase, which differs from the mixed seepage of water and oil phases in reservoirs. Therefore, by simulating simultaneous oil-water seepage in the same formation layer, the water cut of the produced fluid from mixed oil-water seepage under the same pressure was tested. The schematic diagram of the experiment is shown in Figure 3.

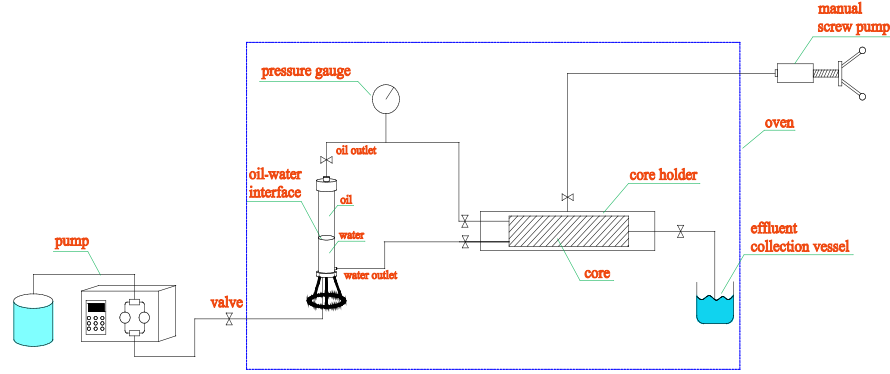


Figure 3 Schematic diagram of the oil-water isobaric co-seepage experiment

The experimental procedures are as follows: ① Under a constant temperature of 70 °C, inject simulated brine into the core at a flow rate of 1.25 mL/min, and measure the permeability, pore volume (PV) and porosity. ② Adjust the flow rate to 0.4 mL/min, and inject oil and water into the core simultaneously. ③ Monitor the injection pressure and the volumes of oil phase and water phase in the produced fluid in real time before RPM solution treatment, and calculate the water cut of the produced fluid. ④ Inject RPM solution into the same core in the reverse direction, and incubate it in a constant temperature chamber at 70 °C for 24 h. ⑤ Inject oil-water mixture into the core at the same flow rate (0.4 mL/min), monitor the injection pressure and the volumes of oil phase and water phase in the produced fluid in real time after RPM solution treatment, and calculate the water cut of the produced fluid.

1.2.8 Aging Stability Test

After injecting 10 PV of RPM solution, the core was sealed and aged for a specified period at a constant temperature of 70 °C, followed by the measurement of oil-phase and water-phase permeabilities. The experimental procedures are as follows:

Procedures ①-④ refer to Section 1.2.7.1; ⑤ The core was sealed and aged for a specified period at a constant temperature of 70 °C; ⑥ Water was injected in the forward direction until the pressure stabilized, and the water-phase permeability K_{w2} was measured; ⑦ Oil was injected in the forward direction until the pressure stabilized, and the oil-phase permeability K_{o2} was determined.

The flow rate for RPM solution injection was 0.4 mL/min, while the flow rate for all other displacement steps was 1.25 mL/min.

2 Results and Analysis

2.1 Fourier Transform Infrared Spectroscopy and Proton Nuclear Magnetic Resonance

The functional group structures of four relative permeability modifiers (HPAM, RPM-I, RPM-II and RPM-III) were characterized by Fourier transform infrared spectroscopy (FT-IR), and the corresponding spectra are shown in Figure 3. The absorption peak near 3450 cm^{-1} is attributed to the N-H stretching vibration of amide groups. The characteristic peak at 2920 cm^{-1} corresponds to the asymmetric stretching vibration of methylene groups ($-\text{CH}_2-$) in the main and side chains of the polymer. The characteristic peak around 1632 cm^{-1} arises from the C=O stretching vibration of amide groups. The absorption peak near 1450 cm^{-1} is formed by the superposition of two vibration modes: one is the stretching vibration of the C-N^+ bond in quaternary ammonium cationic groups, and the other is the bending vibration of C-H bonds in long-chain alkyl segments.

No obvious absorption response is observed for the HPAM sample at this wavenumber, whereas prominent characteristic peaks appear in the spectra of RPM-I, RPM-II and RPM-III. Combined with the monomer feeding composition, it is confirmed that cationic adsorptive groups are successfully grafted onto the molecular chains of RPM-I, and hydrophobic associating groups are successfully grafted onto the molecular chains of RPM-II. In addition, distinct absorption peaks of S=O stretching vibration appear near 1039 cm^{-1} for all four RPMs, indicating that sulfonic acid groups are successfully incorporated into the molecular chains of all four samples.

To further verify the molecular structure and functional group grafting effect of the polymers, ^1H nuclear magnetic resonance spectroscopy (^1H NMR) was applied to characterize the four samples, with deuterated water (D_2O) as the solvent. The obtained ^1H NMR spectra are displayed in Figure 4. The signal at $\delta \approx 4.7\text{ ppm}$ is the solvent proton peak of deuterated D_2O . The signal at $\delta \approx 3.72\text{ ppm}$ (f) is assigned to the proton absorption of methylene groups adjacent to the ester oxygen ($-\text{COO}-\text{CH}_2-$) in the side chains of cationic adsorptive groups. The signal at $\delta \approx 3.6\text{ ppm}$ (g) corresponds to the protons of methylene groups directly linked to sulfonate groups ($-\text{CH}_2-\text{SO}_3-$) in AMPS.

The characteristic peak at $\delta \approx 3.37$ ppm (h) is attributed to the protons of methylene groups directly bonded to N^+ (N^+-CH_2). The characteristic peak at $\delta \approx 3.15$ ppm (i) corresponds to the protons of methyl groups directly bonded to N^+ (N^+-CH_3). The signal at $\delta \approx 2.10$ ppm (j) arises from the protons of α -methylene groups adjacent to carbonyl groups. The absorption peaks at $\delta \approx 1.59$ ppm (k) and 1.40 ppm (l) originate from the proton response of segments close to functional groups (e.g., β -methylene groups). The characteristic peak at $\delta \approx 1.20$ ppm (m) is the proton signal of methylene groups in long-chain alkyl segments far from polar functional groups.

Comparative analysis of the spectra shows that HPAM exhibits no characteristic proton peak of quaternary ammonium methyl groups at $\delta = 3.15$ ppm, while both RPM-I and RPM-III show prominent proton responses at this chemical shift, and characteristic absorption peaks of methylene groups adjacent to ester bonds also exist at $\delta = 3.72$ ppm for both samples. Combined with the monomer feeding composition and FT-IR characterization results, it is confirmed that quaternary ammonium cationic adsorptive groups are successfully introduced into the molecular chains of both RPM-I and RPM-III. In addition, no characteristic signal of long-chain alkyl methylene groups ($\delta \approx 1.20$ ppm) is detected in the ^1H NMR spectrum of RPM-I, whereas obvious proton absorption appears in this chemical shift region for RPM-II and RPM-III, verifying that hexadecyl hydrophobic associating functional groups are successfully grafted into their molecular backbones.

In summary, the characterization results of FT-IR and ^1H NMR are in good agreement with each other, confirming that the actual molecular structures of HPAM, RPM-I, RPM-II and RPM-III are fully consistent with the pre-designed molecular architecture, and all target functional groups are successfully grafted onto the polymer backbones.

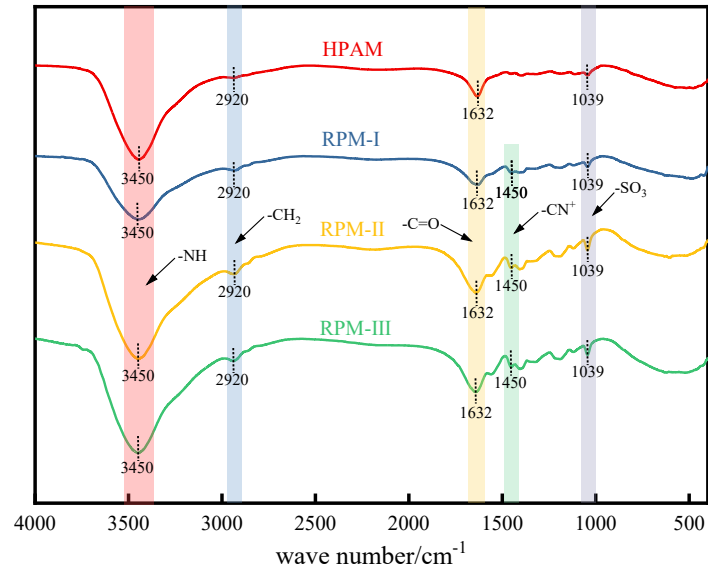


Figure 3 FTIR spectrum f RPM

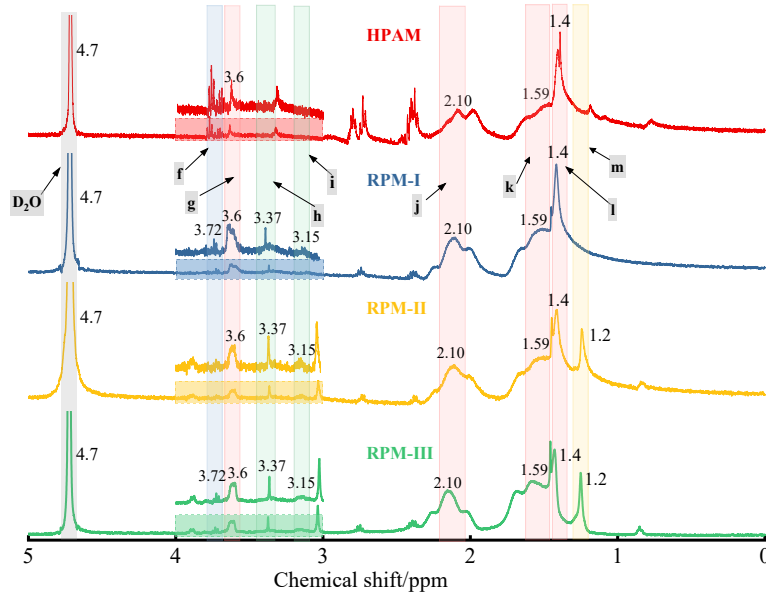


Figure 4 ^1H NMR spectrum of RPM

2.2 Injectivity and Working Mechanism of Relative Permeability Modifiers

2.2.1 Injectivity and Effluent Concentration Detection of Relative Permeability Modifiers

The injectability of relative permeability modifiers (RPMs) into the target reservoir zone for water control is a prerequisite for their relative permeability modification performance. Accordingly, the injection pressure gradient growth rate λ was adopted as the evaluation metric in this experiment. Combined with the variation

of core seepage resistance and the retention rate of RPM concentration in the effluent, the injectivity differences among RPMs with distinct molecular structures were investigated, and the injection performance was further verified by the RPM concentration in the produced fluid.

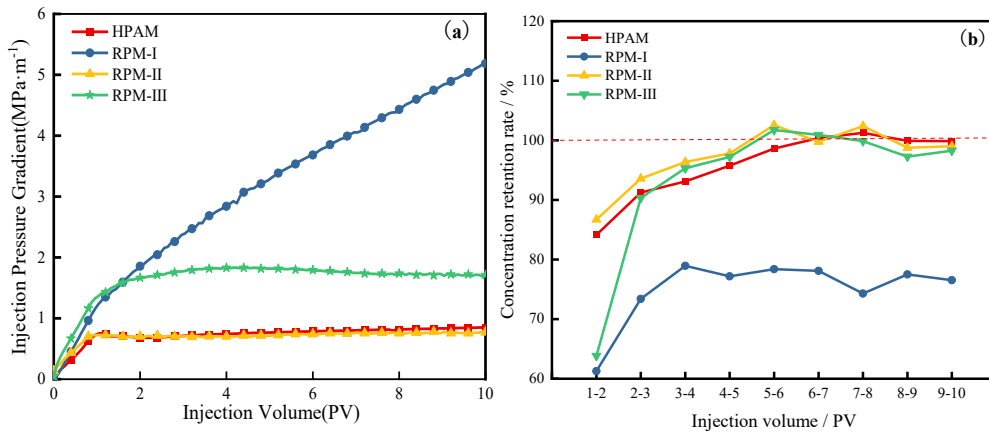
As shown in Table 5 and Figure 6, HPAM and hydrophobically associating RPM-II exhibit outstanding injectivity, with injection pressure gradient growth rates λ of 0.17 and 0.10, respectively. The injection pressure gradient stabilizes rapidly within an injection volume of 1-2 pore volumes (PV), and the effluent concentration retention rate recovers to 100% when the injection volume reaches 4–5 PV. This may be ascribed to the fact that only weak adsorption interactions, including hydrogen bonds and van der Waals forces, exist between these two agents and pore throat walls. Adsorption saturation can thus be achieved within a short time, with no risk of sustained retention and plugging ^[42].

RPM-I presents a markedly high injection pressure gradient growth rate λ of up to 3.82. Its pressure gradient rises linearly with increasing injection volume, and the effluent RPM concentration retention rate remains below 80% for an extended period. This is presumably because cationic groups form strong electrostatic adsorption with the negatively charged rock surface, resulting in excessive adsorption at pore throats and subsequent pore throat plugging, which drives the continuous rise in injection pressure.

RPM-III delivers favorable injection performance, with an injection pressure gradient growth rate λ of 0.26. The injection pressure gradient increases first and then plateaus within an injection volume of 1–3 PV, and the effluent concentration retention rate fluctuates dynamically around 100% after the injection volume reaches 5–6 PV. This indicates that the hydrophobically associating groups in the molecular chains of RPM-III significantly mitigate the poor injectivity issue induced by cationic groups. The underlying mechanism is likely that the hydrophobically associating groups on molecular chains strengthen intermolecular interactions via hydrophobic association, reduce the propensity of individual molecules to adsorb onto the rock surface after detaching from the bulk solution, and effectively attenuate the adsorption retention capacity.

Table 5 Injectivity performance of relative permeability modifiers

Relative permeability modifier	Injectivity			
	$P_1/\text{MPa}\cdot\text{m}^{-1}$	$P_2/\text{MPa}\cdot\text{m}^{-1}$	λ	Injectivity grade
HPAM	0.75	0.88	0.17	Excellent
RPM-I	1.21	5.83	3.82	Poor
RPM-II	0.72	0.79	0.10	Excellent
RPM-III	1.32	1.66	0.26	Excellent

**Figure 6 Injection pressure gradient curves (a) and effluent concentration retention rates (b) of different relative permeability modifiers**

2.2.2 Hydrodynamic Diameter of Relative Permeability Modifiers

The adsorption retention of relative permeability modifier (RPM) solutions in cores can be divided into two components: adsorption on pore surfaces and mechanical retention induced by pore throats. Accordingly, this section indirectly analyzes and discusses the mechanical retention of RPMs in cores based on the hydrodynamic size results of RPMs (Figure 7).

The main peak of the particle size distribution of HPAM is approximately 100 nm, with a narrow distribution range and no distinct characteristic peak of aggregates. This indicates that this linear polymer mainly exists in an extended single-molecule conformation in solution, featuring a low degree of molecular aggregation and uniform hydrodynamic size. The main peak particle size of RPM-I increases to around 1000 nm. This is presumably because the molecular chains carry both cationic groups and anionic groups ($-\text{COO}^-$ and $-\text{SO}_3^-$), which drive the formation of large-scale aggregates between molecular chains via electrostatic attraction. The main peak particle size of RPM-II reaches 3000 nm, far exceeding that of HPAM and RPM-I. This arises from the intermolecular association generated by hydrophobic groups on RPM-II molecular

chains, which forms large-sized supramolecular network structures. It can also be inferred that the intermolecular hydrophobic association force is stronger than the electrostatic attraction between molecular chains, which accounts for the larger hydrodynamic size of RPM-III (with similar molecular weight) compared with RPM-II. The main particle size peak of RPM-III is approximately 3000 nm, comparable to that of RPM-II, which further confirms that intermolecular association plays a dominant role in increasing the hydrodynamic size of RPMs.

The artificial core used in the aforementioned injectivity tests (permeability $\approx$ 200mD, porosity $\approx$ 35%) has a pore throat diameter of approximately $4\mu\text{m}$ ^[43], which is much larger than the hydrodynamic sizes of the four RPMs. This indicates a low probability of mechanical retention for all four RPMs in the artificial core, and further verifies that the poor injectivity of RPM-I in the artificial core is caused by excessive adsorption induced by cationic groups in its molecular chains. In addition, HPAM and RPM-II exhibit similar growth trends in injection pressure, but their hydrodynamic sizes differ by nearly 30-fold. This demonstrates that the adsorption mechanism of RPM-II on pore throat walls is similar to that of HPAM (dominated by hydrogen bonds, van der Waals forces, etc.), and no mechanical retention occurs due to large molecular aggregates.

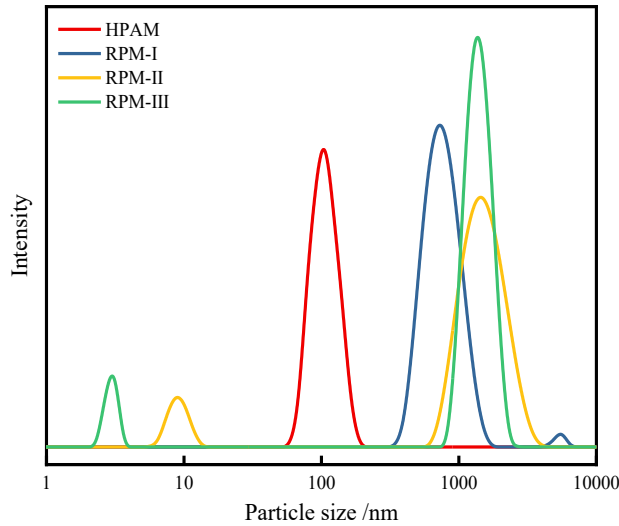


Figure 7 Particle size distribution profiles of different relative permeability modifiers

2.3 Interaction between Relative Permeability Modifiers and Sandstone Surfaces

2.3.1 Desorption Resistance Performance

The firm adsorption of relative permeability modifiers (RPMs) onto pore throat

walls is critical for them to further exert their oil stabilization and water control effects. Accordingly, this section further investigates the interaction mechanism between the four RPMs and rock surfaces via desorption resistance evaluation.

As can be seen from Figure 8, RPM-I, RPM-II and RPM-III exhibit strong adsorption capacity and desorption resistance, whereas HPAM does not possess such properties. Analysis indicates that the positively charged segments formed by cationic groups in RPM-I molecular chains can generate strong electrostatic interactions with negatively charged quartz sand surfaces, promoting the direct adsorption of a large number of molecular chains onto the quartz sand surfaces. In addition, a small fraction of molecular chains are indirectly adsorbed onto the quartz sand surfaces via intermolecular electrostatic interactions.

The interaction force between RPM-II and quartz sand is similar to that of HPAM, with a small number of molecular chains directly adsorbed on the quartz sand surfaces. In contrast, RPM-II can be indirectly adsorbed onto quartz sand surfaces through intermolecular hydrophobic association. Moreover, the intermolecular hydrophobic association is stronger than the intermolecular electrostatic interaction between molecular chains described for RPM-I, which endows RPM-II with an adsorption capacity comparable to RPM-I but a relatively weaker desorption resistance.

The adsorption mechanism of RPM-III is similar to that of RPM-I. However, the intermolecular hydrophobic association present in RPM-III greatly inhibits the excessive adsorption between the positively charged segments in its molecular chains and the quartz sand surfaces. As a result, part of its molecular chains are directly adsorbed onto the quartz sand surfaces via electrostatic interactions, while the other part are indirectly adsorbed via intermolecular hydrophobic association, thus presenting strong adsorption capacity and desorption resistance.

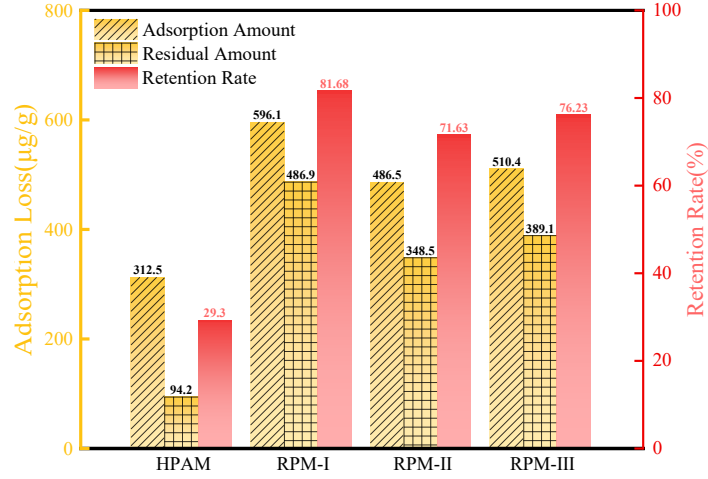


Figure 8 Relationship between adsorptive group content, static adsorption performance and desorption resistance of different relative permeability modifiers

2.3.2 Cryo-SEM Scanning of RPM Adsorption Layers

Cryo-SEM scanning directly visualizes the morphological differences in the adsorption layers of different relative permeability modifiers (RPMs) on capillary wall surfaces, providing direct microscopic evidence for interfacial adsorption behavior. In this experiment, smooth glass capillaries with uniform pore size were employed. After aqueous phase flushing, free RPM molecules inside the capillaries were washed out, and only polymer molecules adsorbed onto the wall surfaces could remain stably. This experiment authentically reflects the wall adsorption performance of various RPMs.

As shown by the cryo-SEM characterization results in Figure 9, HPAM (Figure 9a) and RPM-II (Figure 9c) only form a small number of scattered, thin and discontinuous adsorption patches on the wall surfaces, failing to form effective adsorption layer coverage. This indicates that the adsorption forces of the two agents on pore throat walls are weak, and desorption is highly prone to occur under water flow scouring.

RPM-I (Figure 9b) forms a dense adsorption structure with pronounced agglomeration and stacking features on the tube wall. This phenomenon verifies that excessive adsorption induced by the strong electrostatic interaction of cationic adsorptive groups in the molecular chains is the core cause for the continuous rise of injection pressure during injection and eventual pore throat bridging and plugging.

In contrast, RPM-III (Figure 9d) forms a uniform and dense continuous adsorption layer without excessive agglomeration or stacking. This reflects the synergistic regulation effect of cationic adsorption and hydrophobic association, which achieves effective adsorption while avoiding pore throat plugging.

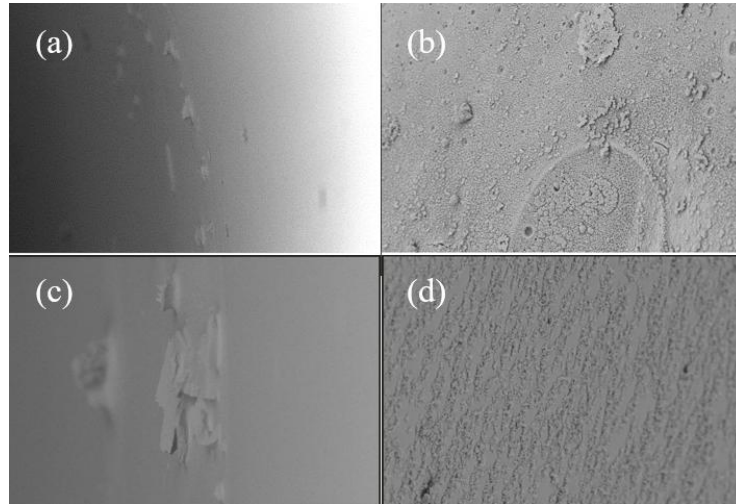


Figure 9 Cryo-cross-sectional images of capillaries for different relative permeability modifiers (a: HPAM; b: RPM-I; c: RPM-II; d: RPM-III)

2.4 Oil Stabilization and Water Control Performance of Relative Permeability Modifiers

2.4.1 Variations in Oil/Water Phase Permeability

The core function of relative permeability modifiers (RPMs) is to achieve selective water plugging without impairing oil flow after being injected into the reservoir. By testing the seepage resistance of water and oil before and after RPM treatment, the water plugging rate and oil plugging rate of RPMs are determined, so as to quantify the differential plugging capacity of RPMs for water and oil phases. On this basis, extensive water flooding is further performed to verify the long-term effectiveness of RPMs in controlling reservoir pore throats.

Figure 10a presents the water plugging capacity of cores treated and modified by four RPMs respectively. After treatment with HPAM and RPM-II, the initial water plugging rates of the cores are both below 50%, indicating weak plugging performance. After extensive simulated brine flushing (60 PV), the water plugging rates drop to less than 34%, with a reduction of over 12%, demonstrating poor long-term stability and insufficient water blocking capacity. Apparently, this is inconsistent with the desorption test result that the adsorption capacity of RPM-II is higher than that of HPAM. Combined with the cryo-SEM scanning results of capillary adsorption, analysis indicates that RPM-II has insufficient adsorption and anchoring capacity on sandstone pore walls, which cannot withstand continuous water flow scouring. This further confirms that the interaction force between RPM-II and rock walls is similar to that of

HPAM.

For the core treated with RPM-I, the initial water plugging rate reaches 92.95%, and after 60 PV of brine flushing, the rate only decreases by 1.79%. This indicates that the RPM-I treated core possesses extremely strong water blocking capacity and long-term effectiveness. For the core treated with RPM-III, the initial water plugging rate is 68.72%, and it drops to 53.63% after 60 PV of brine flushing, with a reduction of 15.09%. Although it still maintains considerable water blocking capacity, its long-term performance needs to be improved. It can be seen that the positively charged segments formed by cationic groups in the molecular chains exert a remarkable positive effect on the adsorption and anchoring of RPMs on sandstone pore walls, and guarantee the long-term water blocking capacity to a certain extent.

Figure 10b illustrates the oil plugging capacity of cores treated and modified by four RPMs respectively. The HPAM-treated core exhibits low impedance to the oil phase. In contrast, the RPM-I treated core has relatively high oil phase impedance, and the oil plugging rate still reaches 40.38% after 60 PV of brine flushing, which is obviously unfavorable. Combined with the aforementioned results, analysis suggests that without the inhibition of hydrophobically associating groups, the cationic groups in RPM-I molecular chains form dense and firm adsorption with sandstone pore walls. As a result, when the oil phase flows through the pores, the molecular chains undergo insufficient conformational contraction and cannot fully open the flow paths for oil phase passage, leading to a high oil plugging rate.

With the regulation of hydrophobically associating groups, the direct adsorption amount of RPM-III on sandstone pore walls is greatly reduced. Meanwhile, molecular chains indirectly adsorbed via hydrophobic association detach from pore walls under the scouring of water or oil flow, resulting in a relatively low oil plugging rate of the RPM-III treated core. However, after detaching from pore walls under flow scouring, these indirectly adsorbed molecular chains will form "molecular clusters" via hydrophobic association, which migrate with the fluid to pore constrictions and cause plugging. This also explains the relatively high oil plugging rate of RPM-II treated cores, as well as the increase in oil plugging rate of both RPM-II and RPM-III after 60 PV of brine flushing.

It can be concluded that the RPM-III treated core features high water plugging capacity and low oil plugging capacity, presenting favorable oil stabilization and water control performance. Nevertheless, the contents of cationic groups and hydrophobically

associating groups in its molecular chains still need further optimization to enhance the adsorption and anchoring capacity of molecular chains on pore walls and reduce the formation of free "molecular clusters", so as to achieve higher water plugging rate, lower oil plugging rate and improved long-term stability. This will be the priority of our follow-up research.

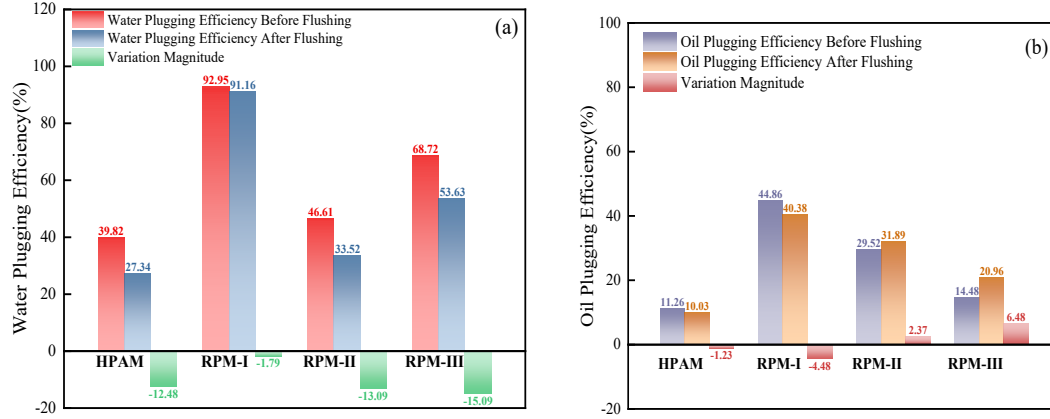


Figure 10 Water/oil plugging rates of different relative permeability modifiers

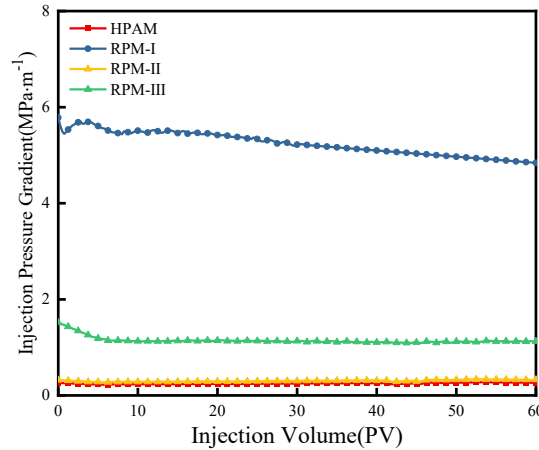


Figure 11 Pressure curves of continuous brine injection after core modification by relative permeability modifiers

2.4.2 Water Cut Test of Produced Fluid under Simultaneous Oil-Water Seepage in the Same Layer

The water/oil phase permeability tests before and after core treatment with relative permeability modifiers (RPMs) are conducted under single-phase flooding conditions, i.e., water phase displacing oil phase or oil phase displacing water phase, which differs from the simultaneous two-phase seepage of water and oil in reservoir formations. Using the method described previously, the simulation of simultaneous oil-water seepage in the same reservoir layer was carried out. The variations of oil and water

phase contents in the produced fluid from cores treated with four different RPMs were measured, to intuitively evaluate the oil stabilization and water control performance of the four RPMs after core modification.

Figure 12 presents the water cut curves of simulated produced fluid under simultaneous oil-water seepage before and after core treatment with RPMs. Before RPM treatment, the water cut of the produced fluid ranges from 55% to 60% within 2–8 pore volumes (PV), with an average water cut of 60.58%. After HPAM treatment, the water cut of the produced fluid within 2-8 PV drops to 50–55%, with an average water cut of 56.93% and a reduction rate of 3.66%. After RPM-II treatment, the average water cut within 2-8 PV is 55.20%, with a reduction rate of 5.39%, which is 1.73% lower than that of HPAM. This may be attributed to the fact that in addition to the HPAM-like behavior of a small number of molecular chains adsorbed on pore walls, the "molecular clusters" formed by free molecular chains swell in water flow and contract in oil flow, facilitating the selective passage of oil and water through pores. At this stage, the "molecular clusters" have not migrated to pore constrictions on a large scale to cause plugging ^[44].

After RPM-I treatment, the average water cut within 2-8 PV is 51.56%, with a reduction rate of 9.02%, demonstrating favorable oil stabilization and water control performance. Although the abundant RPM-I molecular chains adsorbed on pore surfaces achieve highly efficient selectivity for water and oil flowing through pores, they also induce a sharp pressure rise during simultaneous two-phase seepage in the reservoir, which is unfavorable for reservoir production (Figure 13). In addition, RPM-I has poor injectability and cannot achieve deep formation migration.

After RPM-III treatment, the average water cut within 2-8 PV is 48.92%, with a reduction rate of 11.66%, which is 2.65% lower than that of RPM-I. It exhibits superior oil stabilization and water control performance, and the pressure increment during simultaneous two-phase seepage in the reservoir is moderate (Figure 13). This is conducive to stabilizing the fluid production rate of the reservoir and increasing crude oil output. In the follow-up research on optimizing the cationic groups and hydrophobically associating groups in the molecular chains of RPMs, better oil stabilization and water control performance is expected to be obtained.

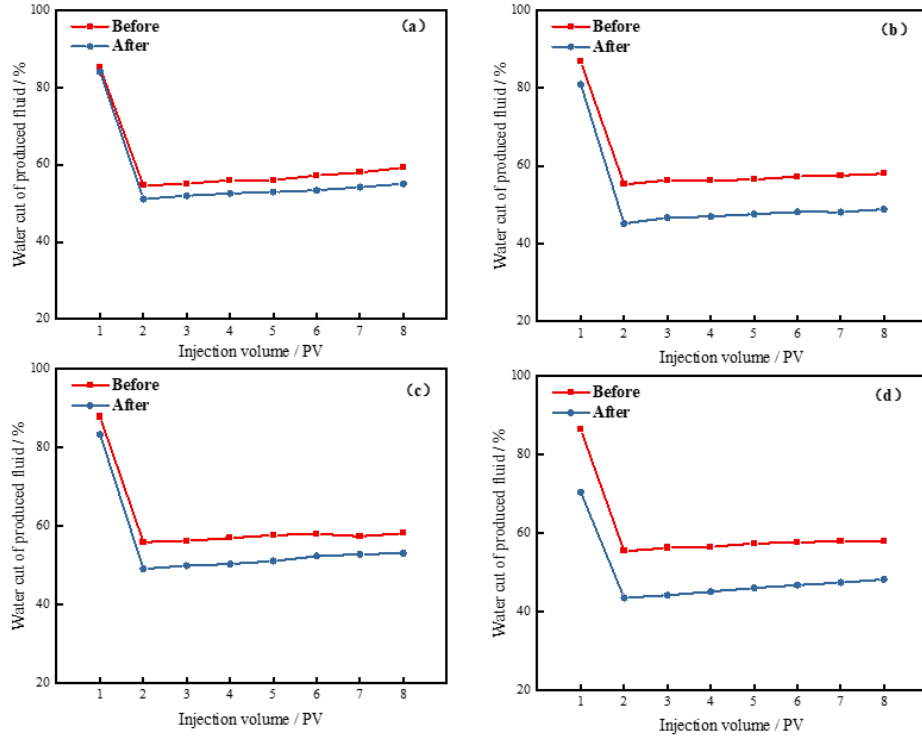


Figure 12 Water cut curves of produced fluid for different relative permeability modifiers:
(a) HPAM, (b) RPM-I, (c) RPM-II, (d) RPM-III

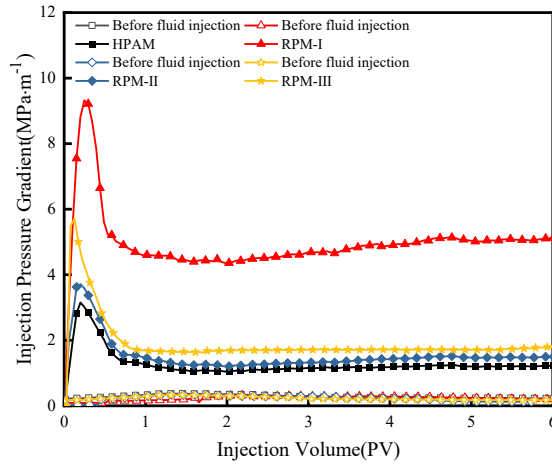


Figure 13 Injection pressure gradient curves under simultaneous oil-water seepage

2.5 Stability of Relative Permeability Modifiers

The high-temperature and high-salinity reservoir conditions pose a severe challenge to polymer molecular chains. Long-term thermal exposure can degrade polymer molecular chains, disrupt associated aggregate structures, and significantly reduce the effective water control lifetime of relative permeability modifiers (RPMs) [45]. In this section, RPM-III was selected as the research object, and thermal stability studies were carried out by statically aging the RPM-III-injected cores at 70°C.

Figure 14 presents the variation patterns of oil and water plugging rates of RPM-

III under different aging times. The results demonstrate that in the early aging stage (0–5 d), the water plugging rate of RPM-III rapidly increases from 62.25% to 73.32%, with an increment of 13.32%, while the oil plugging rate only slightly rises from 12.18% to 14.66%, and the oil-water selectivity ratio remains above 5.0. This is ascribed to the fact that high temperature intensifies the thermal motion of polymer molecules, enhances the contact between free polymer molecules retained in pores and the core surface, and enables them to be fully adsorbed and anchored onto pore walls. Meanwhile, continuous intermolecular contact and collision further strengthen hydrophobic association, reinforcing the adsorption and association structure on the original hydrated adsorption layer and significantly enhancing the aqueous phase plugging barrier ^[46]. In contrast, the increment of the oil plugging rate is limited, indicating that the newly formed hydrated adsorption layer still maintains favorable oil-water selectivity.

In the middle-late aging stage (5–60 d), the water plugging rate increases by approximately 7% compared with the early aging stage. At this point, the adsorption layer thickness tends to stabilize. The high-temperature environment does not cause large-scale degradation of polymer molecular chains or failure of the adsorption layer; instead, a more stable dense hydrated layer is formed through slow structural rearrangement, achieving long-term water control.

Apparently, RPM-III possesses excellent temperature resistance and has the potential to maintain long-term oil stabilization and water control performance in medium-high temperature reservoirs.

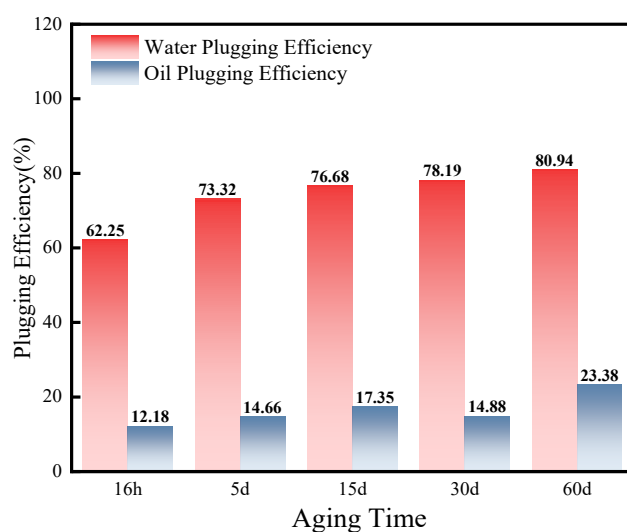


Figure 14 Water and oil shutoff efficiencies of RPM-III after thermal aging

3 Conclusions

(1) Four relative permeability modifiers (RPMs) with distinct molecular structures were synthesized via aqueous free radical polymerization, and their molecular structures were verified to be consistent with the designed configurations via Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectroscopy (^1H NMR).

(2) The differences in injectivity of RPMs with different molecular structures and the underlying mechanisms were elucidated through a series of experiments. It is demonstrated that cationic groups in molecular chains promote the adsorption and anchoring of molecular chains onto pore walls, resulting in insufficient injectivity and deep formation migration capacity. Hydrophobically associating groups can strengthen intermolecular interactions between molecular chains and inhibit the detachment of molecular chains from the bulk solution as well as their subsequent adsorption and anchoring onto pore walls, thereby improving injectivity and deep formation migration capacity.

(3) The mechanisms and performance differences of oil stabilization and water control for RPMs with different molecular structures were clarified via targeted performance evaluation experiments. Molecular chains anchored on pore walls via cationic groups extend when water flows through pores, restricting aqueous phase flow; while they undergo conformational contraction when oil flows through pores, opening flow paths for oil phase passage. However, an excessively high density of molecular chains on pore walls leads to insufficient contraction space for molecular chains, which prevents the full opening of flow paths. Hydrophobically associating groups reduce the molecular chain density on pore walls, enabling sufficient conformational contraction of molecular chains and full release of flow paths. Nevertheless, free molecular chains tend to form "molecular clusters", which migrate with water or oil flow to pore constrictions and cause plugging.

(4) RPM-III, which incorporates both cationic groups and hydrophobically associating groups in its molecular chains, exhibits favorable injectivity ($\lambda=0.26$), oil stabilization and water control performance ($N_w=68.72\%$, $N_o=14.48\%$) and long-term stability. Its injectivity is significantly improved compared with RPM-I bearing solely cationic groups ($\lambda=3.82$); its oil stabilization and water control performance as well as long-term stability are markedly enhanced relative to RPM-II functionalized only with hydrophobically associating groups ($N_w=46.61\%$, $N_o=29.52\%$). Nevertheless, the

contents of cationic groups and hydrophobically associating groups in the molecular chains of RPM-III still require further investigation and optimization to achieve more desirable performance.

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5 Competing interests

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work. There is no professional or other personal interest of any nature or kind in any product, service and company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

6 Author contributions

Jing Kang: Writing-original draft, Writing-review & editing, Conceptualization, Investigation, Formal analysis, Visualization, Data curation.

Yongjun Guo: Writing-review & editing, Conceptualization, Supervision, Validation, Project administration.

Rusen Feng: Conceptualization, Methodology, Supervision.

Jin Cheng: Investigation, Data curation.

Wei Zhang: Investigation, Data curation.

Huabing L: Investigation, Data curation.

Xuejun Wen: Investigation, Data curation.

Haiyan Su: Validation, data verification.

Fengxia Ren: Validation, data verification.

Xi Shi: Validation, data verification.

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