



Original Paper

Double-emulsion fabrication of dual-network PTS microspheres with temperature/salt resistance and delayed swelling: Molecular simulation and deep profile control application in reservoir deep zones

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ABSTRACT

High-temperature and high-salinity (HTHS) reservoirs suffer from strong heterogeneity and well-developed preferential flow channels, leading to low water flooding efficiency. Existing profile control microspheres fail to simultaneously achieve high temperature resistance, salt tolerance and delayed swelling. Herein, temperature-resistant, salt-tolerant and delayed-swelling PTS microspheres with a dual “chemical crosslinking-hydrophobic association” network were synthesized via O/W/O double-emulsion polymerization using acrylamide (AM), sodium styrene sulfonate (NaSS), stearyl methacrylate (SMA18) and divinylbenzene (DVB) as monomers. The PTS microspheres had an average particle size of 4.02 μm with good dispersity, maintained structural integrity after 90 days of aging at 120 $^{\circ}\text{C}$ in $2.5 \times 10^5 \text{ mg L}^{-1}$ brine, and exhibited a swelling ratio of less than 20% at 24 h with a final expansion multiple of more than 14. Molecular dynamics (MD) simulations revealed that PTS possessed a more compact conformation ($R_g = 1.87 \text{ nm}$) and a stable hydrogen bond network than conventional polyacrylamide (PAM), which was the intrinsic molecular mechanism for its superior temperature and salt resistance. Core flooding experiments showed that PTS effectively blocked high-permeability zones and diverted flow to low-permeability zones, increasing oil recovery by 28.3% to a final oil displacement efficiency of 81.4%. This double-emulsion template strategy realizes a synergistic breakthrough in HTHS resistance and delayed swelling, providing a novel high-performance material for deep profile control in HTHS reservoirs.

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1. Introduction

Against the backdrop of continuously growing global energy demand, the efficient development of oil and gas resources has become a crucial issue for ensuring energy security. Currently, over 40% of the world's proven oil and gas reserves (Xiang et al., 2025a) are located in ultra-high-temperature and high-salinity reservoirs with temperatures exceeding 100 $^{\circ}\text{C}$ and salinities above $2 \times 10^5 \text{ mg L}^{-1}$ (Liu et al., 2022; Yang et al., 2016). Prolonged water

flooding in such reservoirs often exacerbates heterogeneity and leads to significant development of preferential flow channels (Feng et al., 2025). This causes injected water to bypass oil-saturated zones, resulting in generally low recovery factors below 25% for the remaining oil, which severely constrains production enhancement (Shehryar et al., 2025; El-Masry et al., 2025).

Deep profile control technology is a key method for improving recovery in such reservoirs (Liu et al., 2025). Its core mechanism involves injecting profile control agents to block high-permeability channels, thereby diverting subsequent fluids into low-permeability zones and enlarging the sweep volume. However, existing profile control systems have notable limitations. Cross-linked gels, while cost-effective, suffer from difficulties in controlling gelation time (Hashemi et al., 2023), susceptibility to

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shear degradation and chromatographic separation, resulting in poor long-term blocking stability (Bai et al., 2024). Preformed particle gels (PPGs) (Suleimanov et al., 2020) offer better salt tolerance, but their particle size is mostly in the millimeter range (Sun et al., 2020), hindering deep penetration into reservoir pore throats. They are also prone to rupture after swelling (Darko et al., 2024). Traditional polyacrylamide (PAM) microspheres face a dilemma (Wang et al., 2016; Yao et al., 2017): excessively rapid swelling can cause near-wellbore blockage, while under high-temperature and high-salinity conditions, severe molecular chain hydrolysis occurs (El-Karsani et al., 2014), preventing reliable long-term plugging.

To overcome these limitations, researchers have attempted to optimize microsphere performance through molecular design (Du et al., 2025; Peng et al., 2024) to achieve good temperature and salt resistance. Examples include topological structure microspheres (Ehtezazi and Washington, 2000), nanocomposite gels (Du et al., 2023), metal ion reinforced dual-crosslinked microspheres (Wang et al., 2018a) and hydrophobically associating microspheres with distinctive salt-tolerant behavior (Yu et al., 2018a). Hou et al. (2017) constructed a double-network microsphere using butyl acrylate, but its temperature resistance was insufficient for 120 °C. Zhao et al. (2014) introduced 2-acrylamido-2-methylpropanesulfonic acid (AMPS) to enhance salt tolerance, yet its stability period in pure water at 120 °C was only 19 days. Zhu et al. (2018) achieved 3-month stability for PAM microspheres at 100 °C via polyethyleneimine (PEI) modification, but the issue of delayed swelling remained unaddressed. These studies indicate that the optimization of a single property fails to simultaneously meet the three core requirements for deep profile control in ultra-deep reservoirs: ultra-high-temperature resistance (>120 °C), high-salinity tolerance (>1.5 × 10⁵ mg L⁻¹), and delayed swelling characteristics.

In recent years, double emulsions (Leister et al., 2023) have emerged as an ideal template for preparing functional micro-materials, owing to their core advantages of multi-phase encapsulation (Ding et al., 2018) and precisely tunable structure (Zentner et al., 2019). The O/W/O type double emulsion, formed via a two-step emulsification (Ding et al., 2018) process, can create a stable layered structure (Zhi et al., 2023) providing isolated micro-environments for active components. Menzel et al. (2013) proposed a novel strategy for synthesizing micron-sized core-shell particles: using a water-in-oil-in-water (W₁/O/W₂) double emulsion as a template, simultaneously polymerizing the inner aqueous phase and the middle oil phase to form a cross-linked poly (4-tbSty-co-DVB) porous hydrophobic shell. An “oil phase locking” mechanism, where the oil phase gels rapidly, reduces mass transfer from the inner to the outer aqueous phase, stabilizing the W₁ droplets. Acrylic acid monomers can selectively destabilize the W₁/O interface, promoting coarsening of the inner aqueous phase and influencing particle formation. Such particles can serve as adsorbents for the simultaneous removal and encapsulation of organic and inorganic cationic substances from aqueous solutions. Currently, research on applying the double emulsion method to synthesize microspheres for oilfield applications remains relatively scarce. Nevertheless, despite the significant progress achieved in microsphere design through molecular-level optimization, existing systems still lack effective strategies to precisely regulate the internal microstructure from the source of structural construction. Most reported microspheres are prepared via bulk or solution polymerization, yielding relatively homogeneous internal architectures that offer limited tunability of compartmentalized domains, swelling pathway (Ehtezazi and Washington, 2000), and crosslinking density gradients. This limitation fundamentally restricts the simultaneous optimization of

temperature resistance, salt tolerance, and delayed swelling behavior within a single material system. In this context, the double emulsion templating approach emerges as a particularly promising strategy, owing to its unique capacity for constructing hierarchical and compartmentalized structures. By creating spatially isolated microenvironments within discrete droplets, the O/W/O double emulsion template enables precise phase segregation of functional monomers, localized crosslinking at compartment boundaries, and controlled diffusion pathways—all of which are difficult to achieve through conventional one-phase polymerization. This templating advantage provides a new strategy to address the aforementioned challenges by enabling rational design of the microsphere architecture from the emulsion construction stage.

Against this backdrop, this study proposes a functional microsphere fabrication strategy based on an O/W/O double-emulsion template. By incorporating temperature- and salt-tolerant functional monomers, rigid crosslinkers and hydrophobic monomers via this template, we successfully constructed a dual-network microsphere structure integrating chemical crosslinking and hydrophobic association characteristics.

This design aims to achieve three core breakthroughs: first, by relying on the spatial confinement effect of the three-dimensional covalent cross-linked network, it effectively suppresses molecular chain degradation under high-temperature conditions, raising the upper service temperature limit of the material to 120 °C; second, with the aid of the anti-ion-shielding effect of the strongly dissociated sulfonate groups (–SO₃H), it can effectively counteract the swelling-suppression effect imposed by a high-salinity environment with concentrations up to 2 × 10⁵ mg/L⁻¹; third, by utilizing the permeation-hindering effect of hydrophobic microdomains, the 24-h swelling ratio of the microspheres is regulated to below 20%, thereby effectively avoiding the risk of near-wellbore blockage.

This work not only provides novel functional material support for deep profile control operations in high-temperature and high-salinity reservoirs, but also offers a universal theoretical and technical framework for the design and development of intelligent responsive plugging materials under extreme operating conditions.

2. Experimental

2.1. Materials

Span80 (analytical grade), acrylamide (AM, 98%), potassium persulfate (KPS, 99%), cyclohexane (analytical grade, 99%), sodium styrene sulfonate (NaSS, 99%), divinylbenzene (DVB, 99%), 2,2'-azobis (2-methylpropionamidine) dihydrochloride (V-50, 99%), white oil (industrial grade), anhydrous ethanol (analytical grade), sodium chloride (NaCl, 99%), potassium chloride (KCl, 99%), magnesium chloride (MgCl₂, 99%), and calcium chloride (CaCl₂, 99%) were all purchased from Shanghai Titan Technology Co., Ltd. YH-R15 (analytical grade) was purchased from Zibo Yonghong New Material Co., Ltd. MOA-3 (industrial grade) was purchased from Jiangsu Hai'an Petrochemical Factory. Deionized water was prepared in the laboratory. Stearyl methacrylate (SMA, 99%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd.

2.2. Experimental methods

2.2.1. Preparation of the O/W/O double-emulsion template

The O/W/O double emulsion was prepared as outlined in Fig. 1(a).

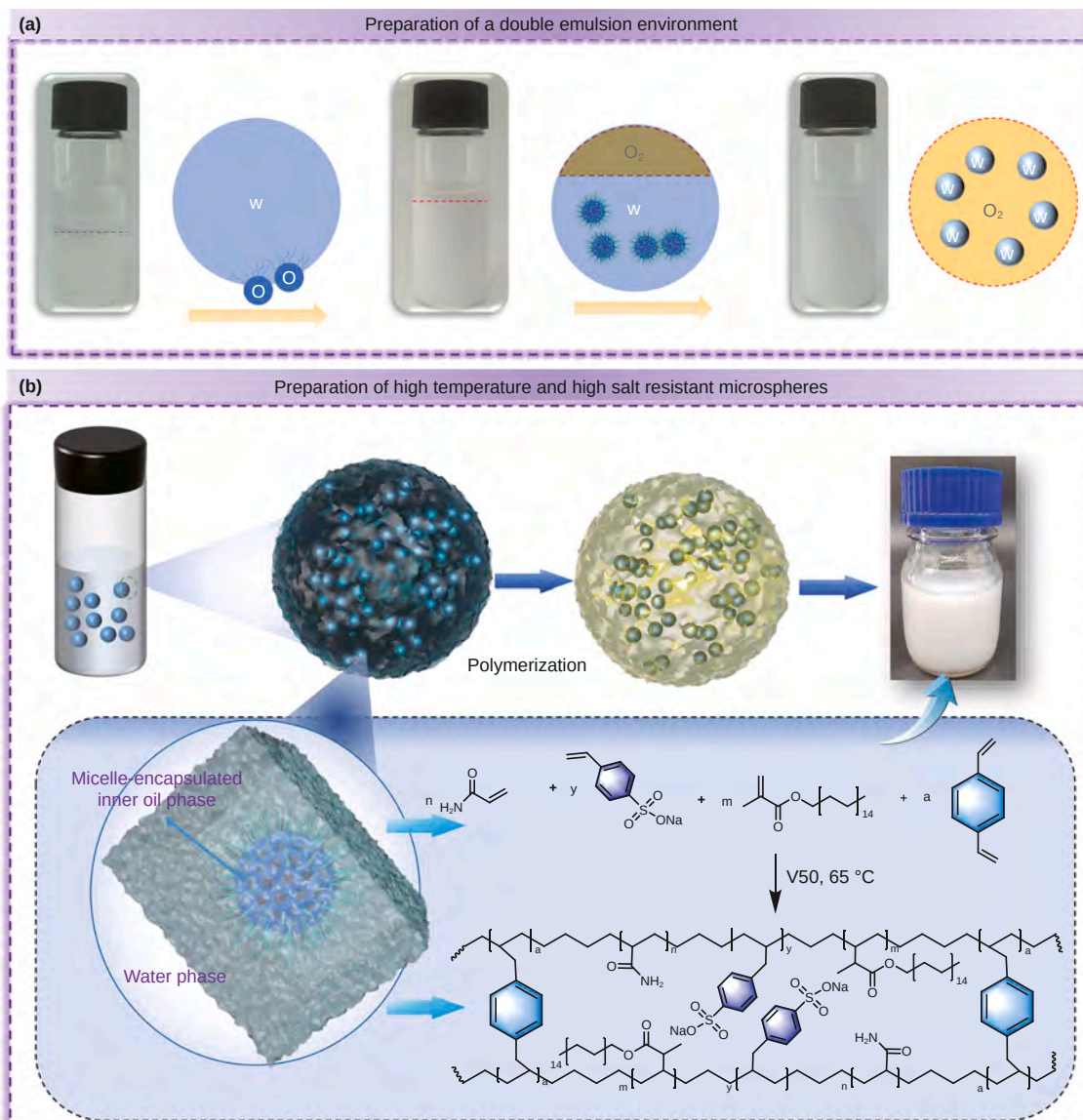


Fig. 1. (a) Preparation flowchart of O/W/O double emulsion template and (b) synthesis process diagram of temperature-resistant, salt-tolerant and delayed-swelling microspheres.

The inner oil phase (O_1), consisting of 10.00 g of white oil, and the aqueous phase (W), prepared by dissolving 0.40 g of YH-R15 emulsifier in 15.00 g of deionized water, were separately sonicated to achieve uniform dispersion. Under magnetic stirring, the W phase was slowly added dropwise to the O_1 phase at an O_1 : W volume ratio of 1:1.5. Stirring was continued at an optimized speed of 5000 rpm for 10 min to produce an O_1 /W primary emulsion with an optimal balance of stability and droplet size. Subsequently, the outer oil phase (O_2) was prepared by dissolving 1.00 g of Span80 (HLB = 4.3) and 1.00 g of MOA-3 (HLB = 7–8) in 54.00 g of cyclohexane. This emulsifier combination, based on the principle of complementary hydrophilic-lipophilic balance (HLB) values, synergistically stabilized the double interfaces. This approach effectively overcame the interfacial film weakening at high temperatures that is characteristic of conventional single-emulsifier systems. Finally, the primary emulsion was slowly added into the O_2 phase at a volume ratio of 1:2. The mixture was then processed in a mechanical oscillator at 400 rpm for 5 min,

ultimately yielding an O₁/W/O₂ double emulsion with excellent thermodynamic and kinetic stability.

2.2.2. Synthesis of the temperature-resistant, salt-tolerant (PTS) microspheres

The microspheres were synthesized following the procedure illustrated in Fig. 1(b). Specifically, 3.00 g of AM, 0.60 g of NaSS, and 0.08 g of V50 were dissolved in the aqueous phase (W), while 0.18 g of DVB and 0.17 g of SMA were added to the inner oil phase (O₁). The system was subsequently mechanically stirred at 500 rpm for 10 min to ensure homogeneity. After purging the double emulsion with high-purity nitrogen for 30 min to remove dissolved oxygen, polymerization was carried out in a 60 °C water bath under stirring at 300 rpm for 1 h. The mixture was then left to age statically for 12 h to ensure a complete reaction. The resulting product was washed three times via centrifugation using a mixture of absolute ethanol and distilled water (1:3, v/v). Finally, it

was air-dried in a fume hood at 40 °C for 24 h to a constant weight, yielding the heat- and salt-tolerant microspheres (PTS).

2.2.3. Synthesis of conventional polymer microspheres (PAM)

Conventional polyacrylamide (PAM) microspheres were prepared via inverse suspension polymerization. First, 42 g of white oil and 7.7 g of OP-10 were mixed uniformly in a 250 mL three-necked flask and purged with nitrogen for 10 min to form the oil phase. Subsequently, 38.6 g of deionized water, 9 g of AM, and 1 g of AMPS were mixed and dissolved. The pH of the solution was adjusted to 7–8 using a 20% NaOH solution, followed by the addition of 0.5 mL of a 2% aqueous solution of N,N'-methylenebisacrylamide (MBA) to prepare the aqueous phase, which was stirred until completely dissolved. This aqueous solution was then slowly added to the three-necked flask using a constant-pressure dropping funnel while stirring at 600 rpm for 1 h. The temperature was then raised to 40 °C, and 0.5 mL of a 3% aqueous solution of ammonium persulfate (APS) and 0.4 mL of a 1% aqueous solution of sodium bisulfite (SHS) were added. The reaction proceeded at 300 rpm for 3 h, resulting in a milky-white emulsion product, i.e., PAM microspheres.

2.3. Chemical structure characterization

Fourier transform infrared spectroscopy (FTIR): Dried microspheres were mixed with KBr at a mass ratio of 1:100, ground, and pressed into transparent pellets. Spectra were recorded in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

^1H nuclear magnetic resonance (^1H NMR): Approximately 50 mg of microspheres were dissolved/dispersed in D_2O via ultrasonication. Spectra were acquired using a 400 MHz NMR spectrometer at 25 °C with 64 accumulations.

2.4. Micromorphology and particle size characterization

Scanning electron microscopy (SEM): Microspheres were dispersed in anhydrous ethanol via ultrasonication for 10 min, dripped onto a silicon wafer, dried, and sputter-coated with a 5–10 nm gold layer. Observations were made at an accelerating voltage of 5–10 kV and a working distance of 8–10 mm. Dynamic light scattering (DLS): Microspheres were dispersed in solution or simulated formation water at a concentration of 0.1% and ultrasonicated for 5 min. Measurements were taken at 25 °C with a 2-min equilibration time, and each sample was measured in triplicate.

2.5. Thermal stability characterization

Thermogravimetric analysis (TGA): Approximately 10–15 mg of dried microspheres were placed in an alumina crucible. Analysis was performed under a nitrogen atmosphere (flow rate 20 mL/min) with a heating rate of 10 °C/min from 25 to 600 °C.

2.6. Specific structural verification

X-ray photoelectron spectroscopy (XPS): Microspheres were uniformly coated onto conductive adhesive and vacuum-dried for 24 h. Analysis was performed using Al $K\alpha$ radiation (1486.6 eV) at a power of 150 W.

2.7. High-temperature stability evaluation

The thermal stability of PTS microspheres was evaluated by aging a 1% PTS microsphere dispersion at 120 °C for 90 days, a temperature corresponding to the maximum temperature of ultra-

deep reservoirs. Both the aging test and the assessment of structural integrity were conducted in accordance with the specified procedures for deep-reservoir polymers in the industrial standard SY/T 7812-2024.

2.8. Salt tolerance performance evaluation

To evaluate the salt tolerance of PTS microspheres, they were dispersed in tap water and simulated formation water with a salinity of $2.5 \times 10^5 \text{ mg L}^{-1}$, respectively. In accordance with the industrial standard SY/T 7812-2024 ((National Energy Administration of China, 2024)), the dispersion stability and particle size variation under different salinity conditions were tested and characterized.

2.9. Delayed expansion performance test

Microspheres were weighed and dispersed in an aqueous solution to prepare 0.5% dispersions of PTS and PAM. These were placed in a constant-temperature oven at 120 °C. Samples were taken periodically, and the particle size distribution was observed using optical microscopy. The swelling ratio was calculated using Eq. (1):

$$\text{Swelling ratio} = \frac{n_1}{n_2} \quad (1)$$

Schott's equation (Wang et al., 2022a) was employed to establish a theoretical model for the microsphere swelling process. Schott's equation is expressed as Eq. (2).

$$\frac{T}{S_{\text{RT}}} = A + BT \quad (2)$$

where A and B are constants. When the duration is sufficiently long ($BT \gg A$), B denotes the reciprocal of the equilibrium swelling time of the microspheres. When $T \rightarrow 0$, A corresponds to the reciprocal of the initial swelling rate of the microspheres.

2.10. Rheological performance evaluation

The shear-thinning characteristics were tested using a rotational rheometer. The viscosity change of the microsphere dispersion was measured at shear rates ranging from 0.1 to 1200 s^{-1} and temperatures from 25 to 120 °C to evaluate shear recovery capability.

2.11. Double-emulsion stability evaluation

To study the stability of the double emulsion, freshly prepared emulsions were stored at room temperature. The volume of the emulsion layer was measured over time, and the creaming index (CI) was calculated to assess physical stability using Eq. (3):

$$\text{CI} = \frac{H_c}{H_t} \times 100\% \quad (3)$$

where H_c is the net height of the emulsion layer, and H_t is the total height of the mixture.

2.12. Profile control and oil displacement performance evaluation of PTS

To evaluate the profile-control performance of PTS microspheres in deep reservoirs, core flooding experiments were conducted using natural cores with a diameter of 2.51 cm and a length

of 10.12 cm. The experimental setup is shown in Fig. 2. The procedure was as follows.

- (1) The core was loaded into a core holder. Confining pressure was applied via a confining pressure pump and maintained 3 MPa higher than the injection pressure throughout the experiment to simulate realistic reservoir conditions and prevent fluid bypass.
- (2) A 2% KCl solution was injected into the core at a rate of 0.25 mL/min until the injection pressure and outlet flow rate stabilized. The initial permeability (K_b) was calculated based on Darcy's law.
- (3) A 0.3 wt% PTS microsphere dispersion was injected until the injection pressure stabilized and microspheres were observed at the outlet.
- (4) The 2% KCl solution was injected again until pressure and flow rate stabilized, and the permeability after plugging (K_a) was measured.
- (5) To simulate reservoir temperature conditions, the core temperature was raised stepwise: first to 80 °C and held for 24 h, then to 120 °C and held for another 24 h. KCl solution flooding (third and fourth rounds) was conducted at each temperature stage. The breakthrough pressure, effluent volume, and oil-saturated volume were recorded to evaluate plugging performance. The plugging effect was comprehensively assessed using parameters such as breakthrough pressure gradient and plugging efficiency (E), calculated using Eq. (4). This also provided a basis for subsequent evaluation of enhanced oil recovery potential. The oil displacement efficiency (η) was calculated using Eq. (5).

$$\eta_1 / \% = V_2 / V_1 \times 100 \quad (4)$$

$$E / \% = K_a / K_b \times 100 \quad (5)$$

where K_b is the initial permeability, μm^2 ; K_a is the permeability after plugging, μm^2 ; V_2 is the volume of oil produced, mL; and V_1 is the initial oil-saturated volume, mL.

2.13. Molecular dynamics (MD) simulation

To further elucidate the temperature-resistant and salt-tolerant mechanism of PTS microspheres synthesized via the double-emulsion method at the molecular level, molecular dynamics (MD) simulations were performed in this work to compare the molecular conformational evolution of PTS and PAM under high-temperature conditions. Simulations were carried out using the GROMACS software package, and system modeling was based on the optimized OPLS force field. For both polymer models, the degree of polymerization (DP) per chain was set to 15. The PTS model consisted of 5 polymer chains, each composed of 6 a.m. units, 4 NaSS units, 3 SMA-18 units, and 2 DVB cross-linking points, with cross-linking established via a random cross-linking algorithm. The PAM model comprised 5 linear polymer chains, each containing 15 acrylamide repeating units. Water molecules were described by the SPC water model, and simulations were conducted at 120 °C (Xu et al., 2024). All simulations were performed in the NPT ensemble. Each system was first equilibrated for 1000 ps, followed by a 100 ns production run. The simulation box was set to 10 nm × 10 nm × 10 nm, with 5 polymer molecules contained in each box. The cutoff radius for van der Waals interactions was set to 1 nm, and Na^+ ions were added to neutralize the system charge. After simulation, quantitative analyses of the polymers were conducted using built-in GROMACS tools.

3. Results and discussions

3.1. Synthesis of PTS microspheres

The temperature-resistant, salt-tolerant, and delayed-swelling (PTS) microsphere is a functional polymeric microsphere based on a dual-network structure of “chemical crosslinking-hydrophobic association”. Its core components include the hydrophobic monomer stearyl methacrylate (SMA-18), the rigid crosslinker divinylbenzene (DVB), the salt-tolerant monomer sodium styrene sulfonate (NaSS), and the backbone monomer acrylamide (AM). The synthesis route and structural schematic are illustrated in Fig. 3(b).

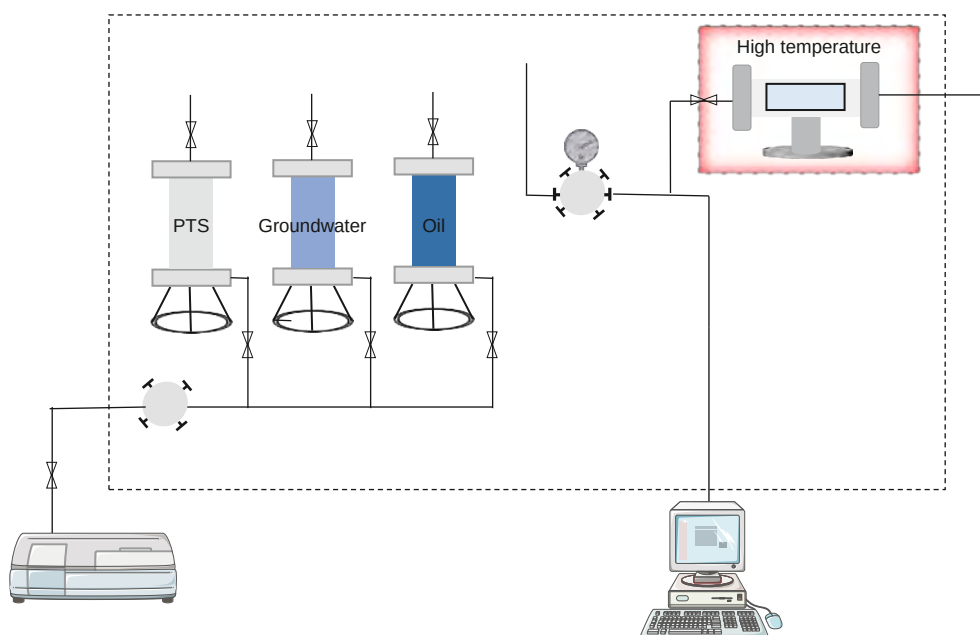


Fig. 2. Schematic diagram of high-temperature sand-packed tube plugging experimental setup.

The PTS microspheres were synthesized via O/W/O double-emulsion polymerization. Within this system, the long alkyl chain of SMA-18 forms dynamic physical cross-linking sites in the polymer network, imparting hydrophobic association characteristics and delayed-swelling properties to the microspheres. DVB acts as the chemical crosslinker, constructing a dense three-dimensional covalent network skeleton that significantly enhances the microspheres' mechanical strength and thermal stability. As a salt-tolerant functional monomer, NaSS provides strongly polar sulfonate groups ($-\text{SO}_3\text{H}$) that effectively counteract the ion shielding effect in high-salinity environments, thereby supplying a sustained driving force for swelling and ensuring colloidal stability. AM serves as the polymer backbone, forming the fundamental framework of the microspheres.

3.2. Microscopic morphology and condition optimization of the double emulsion

The structural integrity of the O/W/O template relies on a tailored hydrophilic-lipophilic balance (HLB) matching strategy and the system's exceptional high-temperature tolerance. A thermally stable surfactant, YH-R15 (HLB = 10), was employed as the primary emulsifier to anchor the outer oil-water interface, effectively inhibiting droplet coalescence during polymerization at 120 °C. Furthermore, by introducing MOA-3 (HLB = 6) as a co-surfactant, a highly dense interfacial film was constructed through their synergistic effect. This rational formulation design fundamentally ensures the structural robustness of the PTS microspheres throughout the entire synthesis and long-term thermal aging processes.

The ratio of the primary emulsion to the outer oil phase is a critical factor affecting the stability of the double emulsion. As shown in Fig. 4(a), no settling occurred at an oil-to-water ratio of 1:2, indicating this ratio is optimal. The change in the creaming index of the emulsion within 1 and 14 days was minimal, demonstrating good stability. The microscopic morphology of the double emulsion was observed using optical microscopy. Fig. 4(b) indicates that when the water-to-oil ratio ($O_1/W/O_2$) of the primary to secondary emulsion was $(1/2)/2$, the emulsion droplets

were more uniform, the internal small droplets were more distinct, and the emulsion stability was better. From Fig. 4(c)–(f), a structure where large droplets encapsulate smaller ones can be observed, preliminarily confirming the formation of a typical double-emulsion structure. Fig. 4(c) illustrates the distribution of the inner oil phase, middle aqueous phase, and outer oil phase within a droplet. The dispersed phase (oil phase, hydrophobic monomer) and the dispersion medium (aqueous phase) form a primary emulsion (O/W), which is then re-dispersed into a second dispersion medium (oil phase, MOA-3) to form a double liquid-liquid dispersion system (O/W/O). The size of the annular liquid film ranges from 10 to 50 μm . As shown in Fig. 4(e), the aqueous phase divides the oil phase into inner and outer parts. Fig. 4(d) shows that the hydrophobic monomer is embedded in the inner oil phase (black region) and isolated from the external reaction reagents (green region) by the liquid film of the middle oil phase (red region). The structure of the double emulsion provides the necessary conditions for the temperature resistance, salt tolerance, and delayed-swelling properties of the microspheres.

3.3. Chemical structure analysis of PTS

From the FTIR spectra shown in Fig. 5(a) and (b), the absorption peak near 1590.58 cm^{-1} indicates the presence of the N–H bending vibration functional group of AM. The absorption peak at 3432.15 cm^{-1} corresponds to the N–H stretching vibration of AM. The absorption peaks near 1455.25 cm^{-1} and 2929.10 cm^{-1} are attributed to the C=C stretching vibration of the benzene rings in sodium styrene sulfonate and divinylbenzene, and the C–H stretching vibration of the aromatic rings, respectively. The absorption peak at 1122.83 cm^{-1} is the characteristic S=O stretching vibration peak of the SO_3^- group in NaSS. The absorption peak at 1628.8 cm^{-1} corresponds to the C=O absorption of stearyl methacrylate. The absorption peak at 643.31 cm^{-1} corresponds to the C–H bending vibration of the vinyl group in DVB. These findings indicate the successful copolymerization of the hydrophobic monomer, salt-tolerant monomer, divinylbenzene, and other monomers, confirming the successful synthesis of PTS.

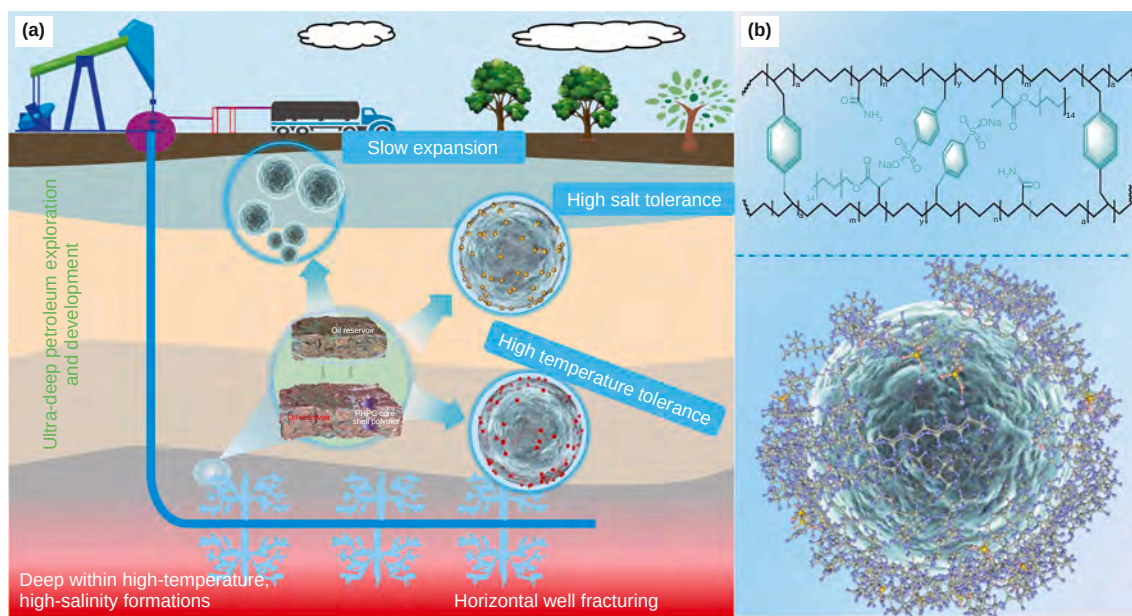


Fig. 3. (a) Schematic diagram of PTS application in ultra-deep hydraulic fracturing and (b) structural schematic diagram of PTS.

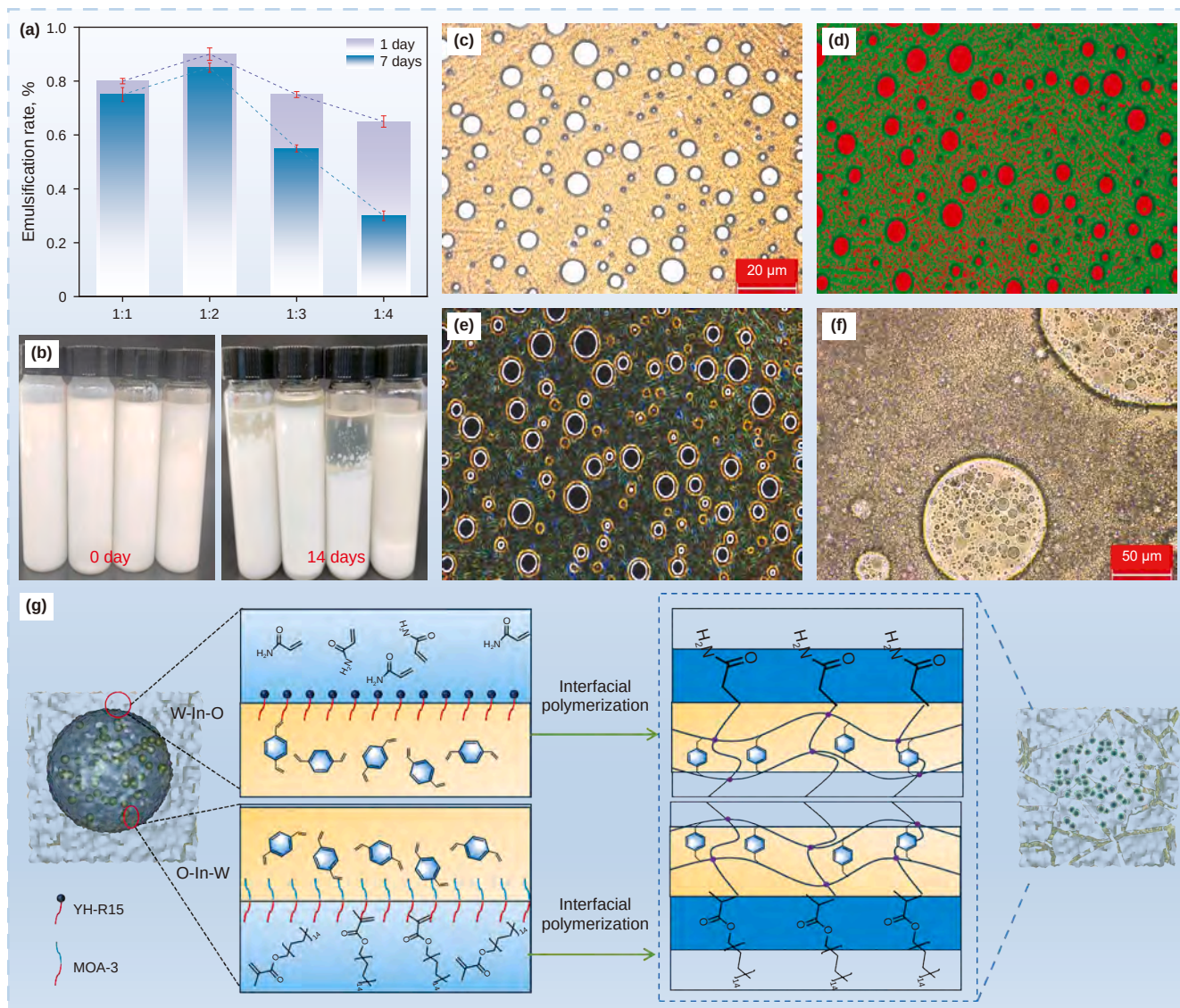


Fig. 4. (a) Emulsification index change of double emulsion at different oil-water volume ratios, (b) double emulsion stability, (c)–(e) micro-morphologies of primary emulsion, (f) micro-morphology of double emulsion, (g) interfacial polymerization mechanism of double emulsion.

Fig. 5(c) displays the TGA curves of the PTS microspheres, whose thermal properties evaluated by thermogravimetric and derivative thermogravimetric analyses show a considerably higher thermal stability margin than conventional polymers. The thermal degradation proceeds in distinct stages: an initial weight loss of only 1.2% from room temperature to 150 °C is mainly attributed to residual solvent volatilization, confirming that the polymer backbone remains fully intact below 150 °C and can reliably endure high-temperature conditions in ultra-deep reservoirs. The major decomposition stage occurs between 150 °C and 450 °C, with a 16.25% weight loss from 150 to 330 °C corresponding to the initial reaction of side-chain functional groups including amide and sulfonate moieties, followed by a sharp 33.12% mass loss from 330 to 400 °C assigned to the cleavage of the carbon main chain, while the extrapolated onset decomposition temperature remains approximately 150 °C. In the slow decomposition stage from 400 to 800 °C, the final residual mass reaches up to 32.2%. This is attributed to the restricted thermal motion of polymer chains by the dense three-dimensional crosslinked network formed by divinylbenzene (DVB), the enhanced backbone bond energy from

the benzene ring structure of sodium styrene sulfonate (NaSS), and the synergistic protective system constructed by long hydrophobic side chains together with ionic and hydrogen-bond interactions.

3.4. Salt-responsive behavior and structural characterization of PTS microspheres

It can be seen from the theoretical model curve of Schott's equation in Fig. 6(a) that the initial swelling rate and equilibrium swelling ratio of PTS may decrease first and then increase. When the salinity is below 10,000 mg/L, the molecular chains of PTS are mainly in a curled conformation, and the swelling rate tends to decrease with the increase of salinity. When the salinity exceeds 10,000 mg/L, hydrophobic chain association of PTS dominates, leading to an increase in the swelling rate with rising salinity.

As shown in Fig. 6(b), compared with conventional polyacrylamide (PAM), PTS microspheres exhibit a unique non-monotonic variation in particle size with increasing salinity. At low sodium chloride concentrations (0–5000 mg/L), the charge shielding effect of sodium and chloride ions compresses the

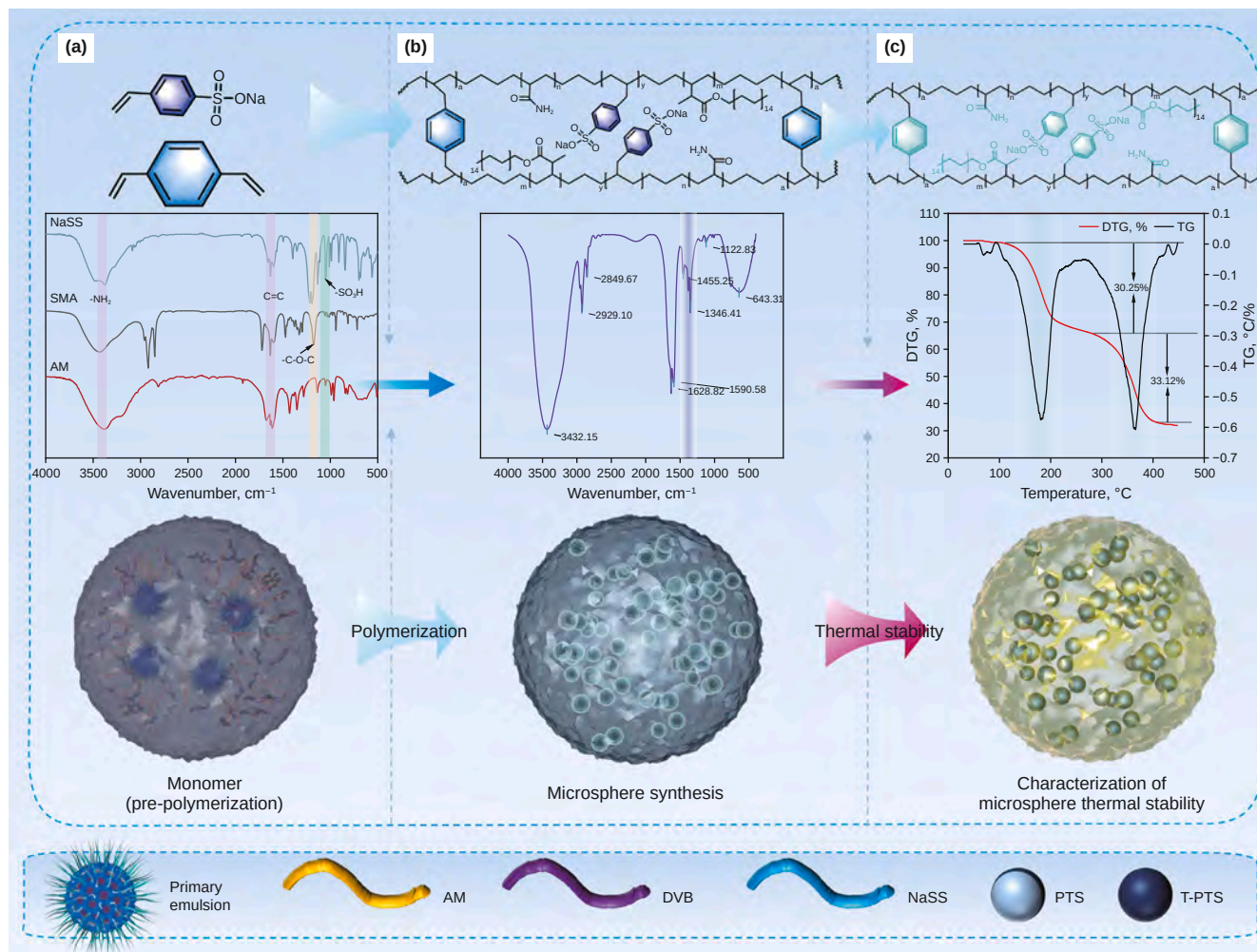


Fig. 5. (a) FT-IR spectrum of PTS before reaction, (b) FT-IR spectrum of PTS after reaction, (c) thermal stability test of PTS.

electric double layer on the outer side of polymer molecular chains and weakens the electrostatic repulsion between sulfonate groups ($-\text{SO}_3^-$). This induces molecular chain contraction and reduces the hydrodynamic particle size. When the salinity further increases to 5000–20000 mg/L, the salting-out effect is significantly enhanced. It preferentially dehydrates hydrophobic SMA segments, promotes intermolecular hydrophobic association, and generates abundant physical crosslinking sites. This salinity-induced hydrophobic aggregation can not only counteract the molecular contraction caused by charge shielding, but also expand the internal network structure through newly formed physical crosslinks, thereby increasing the overall particle size of microspheres. The chemical crosslinking network constructed by divinylbenzene forms a rigid mechanical skeleton and guarantees the colloidal stability of the system during structural rearrangement. Relying on the above mechanism, PTS microspheres retain outstanding plugging performance and structural stability in high-salinity environments, while conventional microspheres usually suffer severe chain contraction under the same harsh conditions.

As shown in Fig. 6(c), the elastic modulus (G') of PTS is consistently higher than its viscous modulus (G'') within the experimental frequency range, indicating that the PTS microsphere dispersion exhibits favorable elasticity. Compared with PAM, PTS exhibits superior performance in both G' and G'' , indicating that it possesses better deformation recovery

capability and stronger erosion resistance under displacement differential pressure. After complete swelling in simulated formation water with a salinity of 2.5×10^5 mg/L, the G' and G'' of PTS reach 8.82 Pa and 2.41 Pa, respectively, which are 1.05 times and 2.97 times the corresponding values of PAM. These results demonstrate that PTS has more excellent viscoelasticity than PAM in high-salinity environments. The viscoelasticity of PTS microspheres can be further enhanced through the interaction between hydrophobic chains inside the microspheres, which can combine with each other to form a new spatial network structure.

As shown in the AFM images (Fig. 6(d) and (e)), the surface morphology and internal network structure of PAM and PTS microspheres differ significantly. Color depth in the images corresponds to surface height, with darker regions indicating lower elevations and lighter regions representing higher peaks.

PAM microspheres shown in Fig. 6(d) exhibit a relatively smooth and uniform surface with gentle undulations. The height ranges from -163.3 to 188.5 nm, which reflects the loose and flexible cross-linked network typical of unmodified polyacrylamide in saline environments. In contrast, PTS microspheres shown in Fig. 6(e) display a markedly rougher and textured surface with pronounced peaks and valleys. The height ranges from -54.1 to 61.6 nm. This increased roughness confirms the formation of a novel rigid dual spatial network structure in PTS,

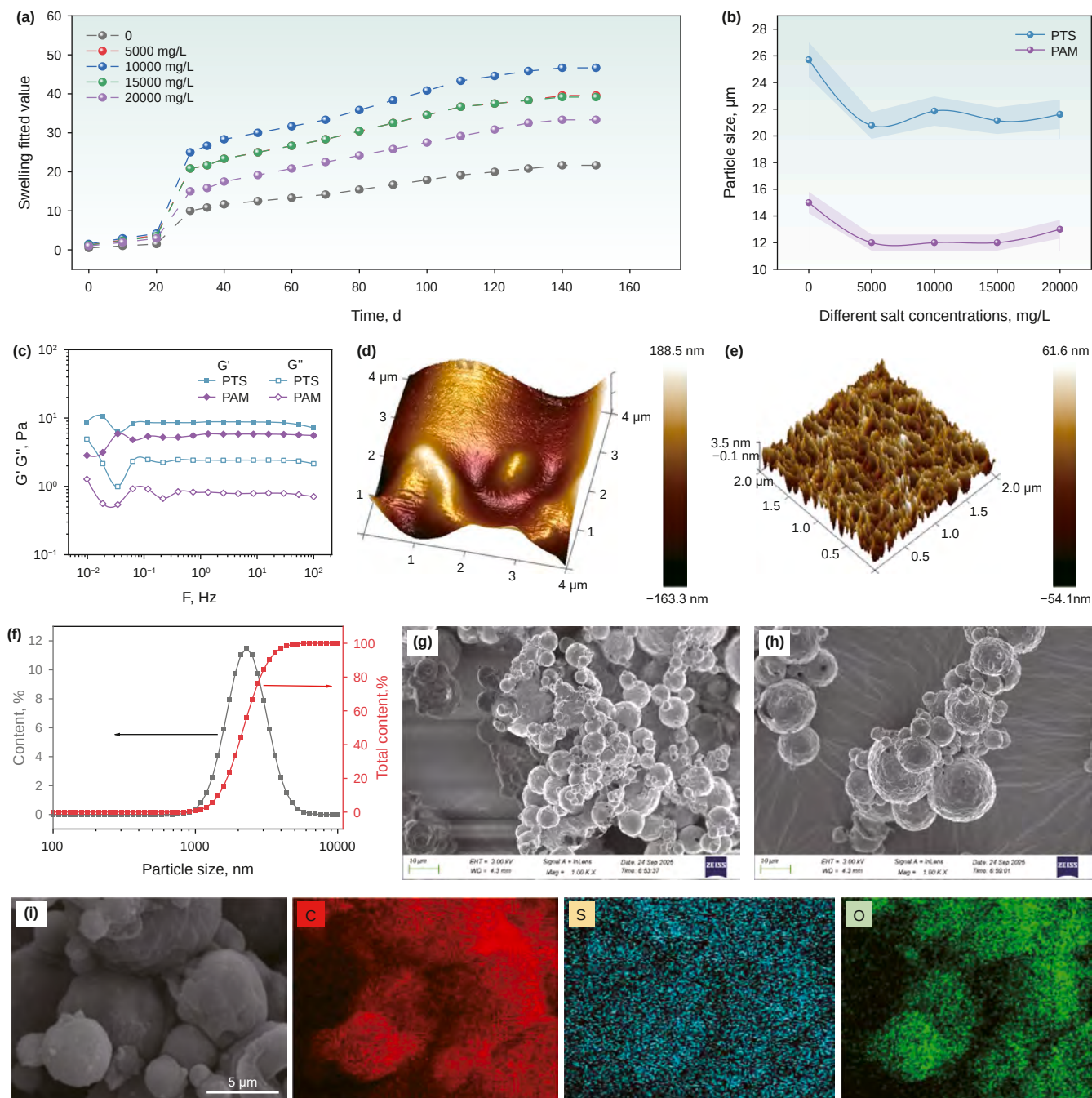


Fig. 6. (a) Fitting curves of PTS swelling kinetics at different NaCl concentrations, (b) viscosity changes of PTS and PAM at different NaCl concentrations, (c) comparison of viscoelastic properties (storage modulus G' , loss modulus G'') between PTS and PAM, (d) atomic force microscopy (AFM) topography of PAM microspheres and (e) PTS microspheres, (f) particle size distribution of PTS microspheres, (g)–(h) surface morphology images of microspheres, (i) element mapping image of microspheres.

arising from modification-induced extra cross-linking points and improved network integrity. These structural changes provide PTS with greater rigidity and stability than PAM, as clearly visualized in AFM topography.

As shown in Fig. 6(f)–(h), the as-prepared PTS microspheres exhibit a regular morphology with uniform spherical shape, slightly rough surfaces and concentrated particle size distribution. DLS characterization indicates that the microspheres show a highly concentrated unimodal distribution with a particle size of 4.02 μm and a polydispersity index (PDI) of 1.013. Wrinkled

structures are observed on the microsphere surfaces in SEM images, which help slow down the penetration rate of water molecules and endow the microspheres with delayed-swelling properties. Overall, these results demonstrate that the PTS microspheres prepared via double-emulsion polymerization possess uniform particle size, well-defined structure, excellent monodispersity, as well as good heat resistance, salt resistance and delayed-swelling. The energy dispersive spectroscopy (EDS) results in Fig. 6(i) confirm that a large amount of carbon (C) and sulfur (S) elements are present on the surface of PTS.

3.5. Chemical structure characterization and specific structure verification of PTS

XPS survey spectra presented in Fig. 7(a) and corresponding high-resolution spectra were employed to determine the chemical composition of PTS. The O 1s spectrum shown in Fig. 7(b) exhibits

an O=C peak at 531.5 eV, attributed to carbon–oxygen double bonds in amide and ester groups, and an O–C peak at 532.8 eV, assigned to carbon–oxygen single bonds in ether or hydroxyl groups. These findings confirm the presence of oxygen-containing functional groups derived from acrylamide and stearyl methacrylate. The C 1s spectrum displayed in Fig. 7(c) reveals a C–C peak

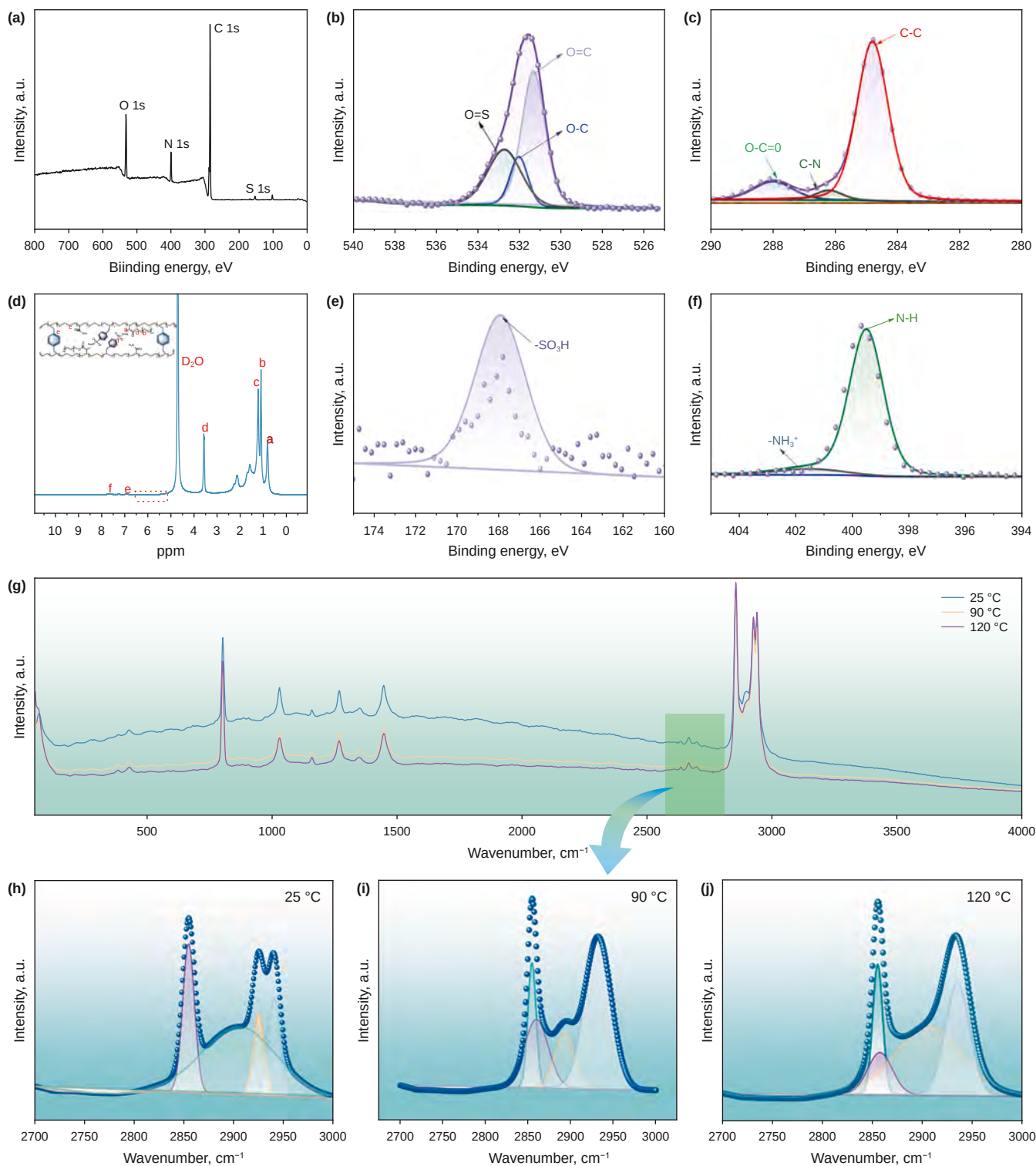


Fig. 7. (a) X-ray photoelectron spectroscopy (XPS) survey spectrum of PTS; high-resolution XPS spectra of (b) C 1s, (c) O 1s, (d) N 1s, and (e) S 2p; (f) ¹H NMR spectrum of the microspheres; (g) raman spectrum of PTS; (h)–(j) detailed fitting of the Raman spectrum for PTS.

at 284.6 eV, corresponding to the carbon chain backbone; an O=C=O peak at 288.8 eV, indicative of ester groups; and a C–N peak near 285.8 eV, reflecting carbon–nitrogen bonds in amide groups. These signals collectively verify the existence of the carbon backbone, amide functionality, and ester moieties. The S 2p spectrum presented in Fig. 7(e) shows an S=O peak at 168.5 eV. With over 95% of sulfur existing in the S=O form, this indicates that sulfonate groups from sodium styrene sulfonate are fully retained in the final product. The N1s spectrum illustrated in Fig. 7(f) displays an N–H peak at 399.8 eV, assigned to amino hydrogen in amide groups originating from acrylamide.

^1H NMR spectra shown in Fig. 7(d) reveal a triplet at 0.80–0.90 ppm attributed to terminal methyl groups in long alkyl chains of SMA. A strong singlet at 1.20–1.30 ppm arises from methylene segments in SMA, confirming incorporation of the hydrophobic monomer. A broad signal at 1.40–2.50 ppm represents the polymer backbone and supports the formation of long-chain polymers. A broad singlet at 1.80–2.00 ppm may be assigned to methyl groups from AM and SMA, though it is partially overlapped by the backbone signal. A broad peak at 6.80–7.20 ppm corresponds to amide groups in AM. A multiplet at 7.10–7.80 ppm is assigned to aromatic protons from NaSS and DVB, confirming successful copolymerization of the salt-tolerant monomer and crosslinker. No obvious sharp peaks appear in the 5.00–7.00 ppm region, indicating full conversion of all vinyl monomers. The size of electrostatic repulsion based on changes in surface charge was further elucidated (He et al., 2025), providing direct proof of the temperature and salt resistance of PTS.

Raman spectroscopy was employed to analyze the molecular structural stability of PTS across different temperatures. As illustrated in Fig. 7(g), the spectral data reveal that with the temperature increasing from 25 to 120 °C, the key characteristic peaks of the material—including the C=O stretching vibration of the AM segment at 1650 cm^{-1} , the aromatic ring vibration of the DVB crosslinking network at approximately 1000 cm^{-1} , and the symmetric and asymmetric S=O stretching vibrations of the NaSS monomer at ~1040 cm^{-1} and ~1190 cm^{-1} —exhibited no significant peak shifts. The peak shapes remained sharp, and the full width at half maximum remained nearly unchanged. Under high-temperature conditions, the chemical bonds and crosslinking network structure of PTS microspheres stayed intact, with no obvious thermal degradation or chemical bond scission observed.

To further clarify the temperature resistance mechanism of PTS microspheres, a focused analysis was performed on the C–H stretching vibrations in the 2700–3000 cm^{-1} region of their Raman spectra as shown in Fig. 7(b)–(e). Signals in this region originate from sp^3 -hybridized C–H bonds in the polymer carbon chain backbone. The analysis revealed high stability of the Raman spectra in this region at 25 °C, 90 °C, and 120 °C: the characteristic peaks at 2850 cm^{-1} and ~2920 cm^{-1} were almost completely overlapping, with a maximum shift of no more than 1 cm^{-1} . This indicates that the bond length and bond energy of C–H bonds remained unchanged under high temperatures, and no thermal oxidative scission or chemical degradation occurred in the carbon chain backbone. The peak shapes remained regular without significant broadening of the full width at half maximum, demonstrating that polymer segments maintained excellent structural orderliness at high temperatures—no substantial short-chain fragments with disordered chemical environments were generated due to chain scission. Additionally, there was no obvious attenuation in the signal intensity of C–H vibration peaks during heating, further confirming that the number of C–H bonds on the carbon chain backbone remained stable and the integrity of the main chain structure was preserved. Consequently, interparticle electrostatic repulsion is significantly enhanced, contributing to

improved system stability (Luo et al., 2023). The results confirm that the prepared PTS possesses the structural characteristics of a temperature-resistant and salt-tolerant material.

3.6. High-temperature stability evaluation of PTS

The high-temperature performance of PTS is presented in Fig. 8(a) and (b), showing that the microspheres initially exist as uniformly dispersed, highly stable white spherical particles at 120 °C. After 30, 60, and 90 days of aging, the emulsion retained its original state without demulsification or sedimentation, demonstrating exceptional thermal stability. As shown in Fig. 8(c), PTS microspheres exhibit outstanding electrochemical stability during aging. Their Zeta potential remains below –32.12 mV (absolute value >30 mV), confirming the presence of a strong electrostatic repulsion barrier on the surface. The TGA and Raman spectroscopy analyses further demonstrate that the chemical cross-linking structure, constructed via DVB covalent bonds, remained thermally stable under thermal stress. This robust covalent skeleton is crucial for inhibiting chain scission of the polymer backbone. As observed through SEM, the microspheres exhibit a complex wrinkled morphology on their surfaces. Combined with the subtle shifts in the characteristic Raman signals associated with hydrophobic association, these results indicate that the internal hydrophobic microdomains (comprised of SMA-18 segments) underwent spatial rearrangement. This structural evolution suggests that while the covalent framework provides mechanical support, the hydrophobic domains dynamically adjust to reach a thermodynamic equilibrium, contributing to the long-term stability of the PTS microspheres.

This outstanding performance can be attributed to the mechanisms illustrated in Fig. 8(d). The three-dimensional crosslinked network structure effectively suppresses the thermal motion of polymer chains, while the rigid aromatic monomers significantly raise the heat deflection temperature of the microspheres. Concurrently, the stable multiple-emulsion interface design facilitates the formation of a dense microsphere shell. Both the intermolecular hydrophobic interactions and covalent crosslinking collectively preserve the structural integrity and dispersion stability of PTS microspheres under high-temperature conditions.

3.7. Salt tolerance and other performance evaluations of PTS

As shown in Fig. 9(a), the prepared PTS microspheres exhibit excellent delayed-swelling properties. In high-temperature and high-salinity conditions, PTS microspheres exhibit only slight swelling within the first 5 d, followed by a slow and sustained swelling process lasting over 48 days, with a final swelling ratio exceeding 14. Fig. 9(b) shows that the zeta potential of PTS microspheres maintains a relatively high negative value (–10 mV to –47 mV) within a salinity range of 0–110,000 mg/L, indicating outstanding colloidal stability. When salinity is below 50,000 mg/L, the absolute zeta potential value remains above 39 mV, indicating a highly stable system. Even at 60,000 mg/L salinity, it reaches –30.25 mV, still within a good stability range. This is primarily due to the high ionization strength and salt resistance of the sulfonate groups in NaSS, which effectively maintain surface charge density and form an electrostatic repulsion barrier (Du et al., 2022). Meanwhile, SMA-18 provides a secondary stabilization mechanism through steric hindrance, preventing microsphere aggregation under high salinity and enabling an intelligent transition from electrostatic stabilization to steric stabilization.

From Fig. 9(c), PTS demonstrates excellent stability during high-temperature aging. After 90 days of aging, the viscosity decreased from 8.5 mPa·s to 8.4 mPa·s at 90 °C, and from 9.1 mPa·s

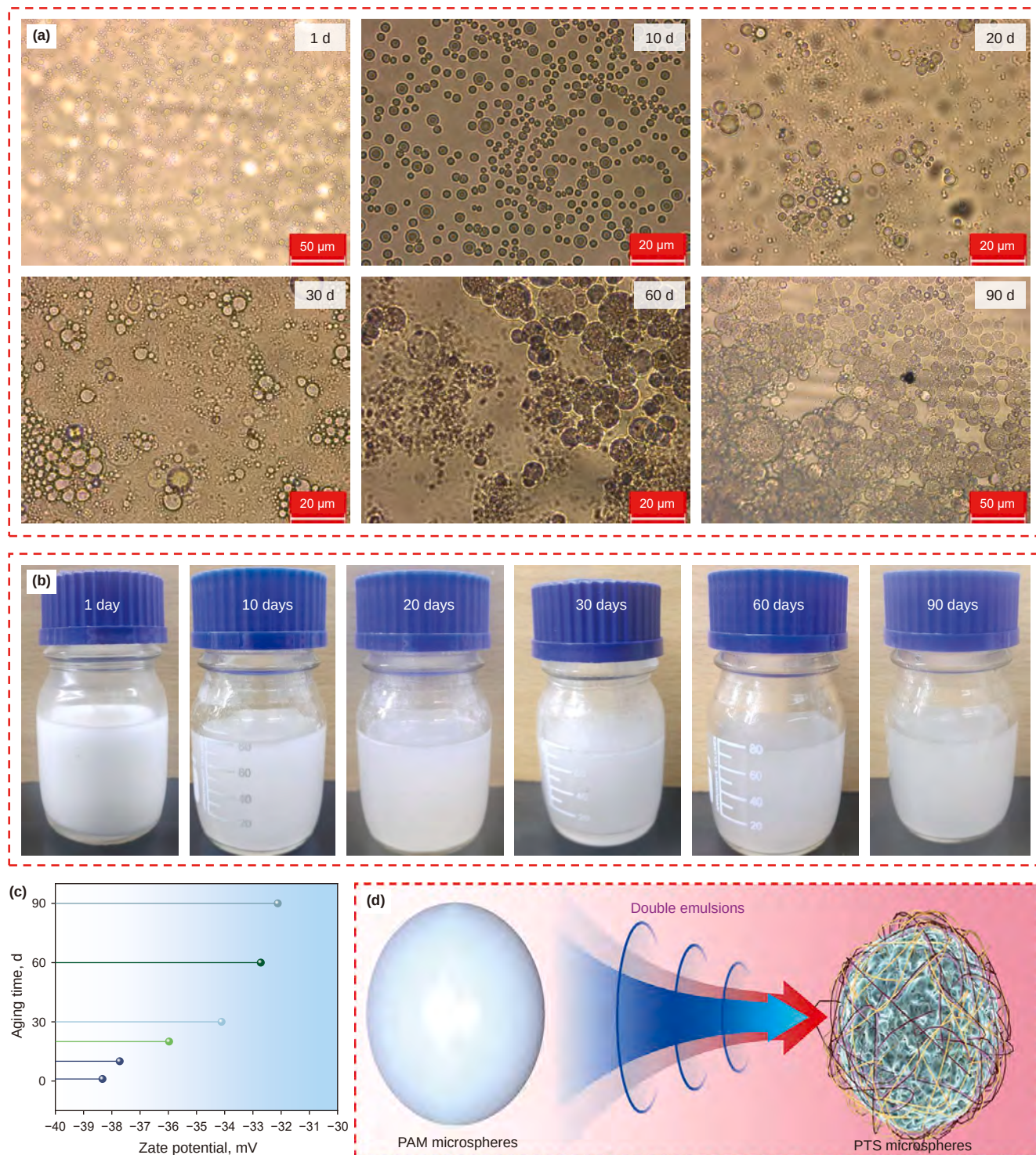


Fig. 8. (a) Microstructure of PTS at 120 °C under different aging times (1 d, 10 d, 20 d, 30 d, 60 d, and 90 d), (b) macroscopic appearance of PTS at 120 °C corresponding to different aging times, (c) zeta potential of PTS microspheres at different aging times, (d) schematic diagram illustrating the comparison between PTS and PAM.

to 8.29 mPa·s at 120 °C, indicating an extremely high viscosity retention rate. According to the rheological performance results shown in Fig. 9(d), the PTS dispersion exhibits typical shear-thinning behavior at different temperatures. As the shear rate increases from 100 s⁻¹ to 1200 s⁻¹, the apparent viscosity decreases significantly, indicating that the microsphere network structure undergoes reversible breakdown under shear, ensuring good injectability.

As shown in Fig. 9(e)–(g), PTS maintains a complete spherical structure under different conditions. Initially, in tap water and high-salinity simulated formation water (2.5×10^5 mg/L), the microsphere diameters are approximately 8.5 μm and 4.3 μm, respectively. After aging at 120 °C for 90 days, the diameters increase to 30.5 μm and 20.1 μm, respectively, with no dissolution or morphological collapse, demonstrating excellent structural stability, temperature resistance, and salt tolerance. Through the

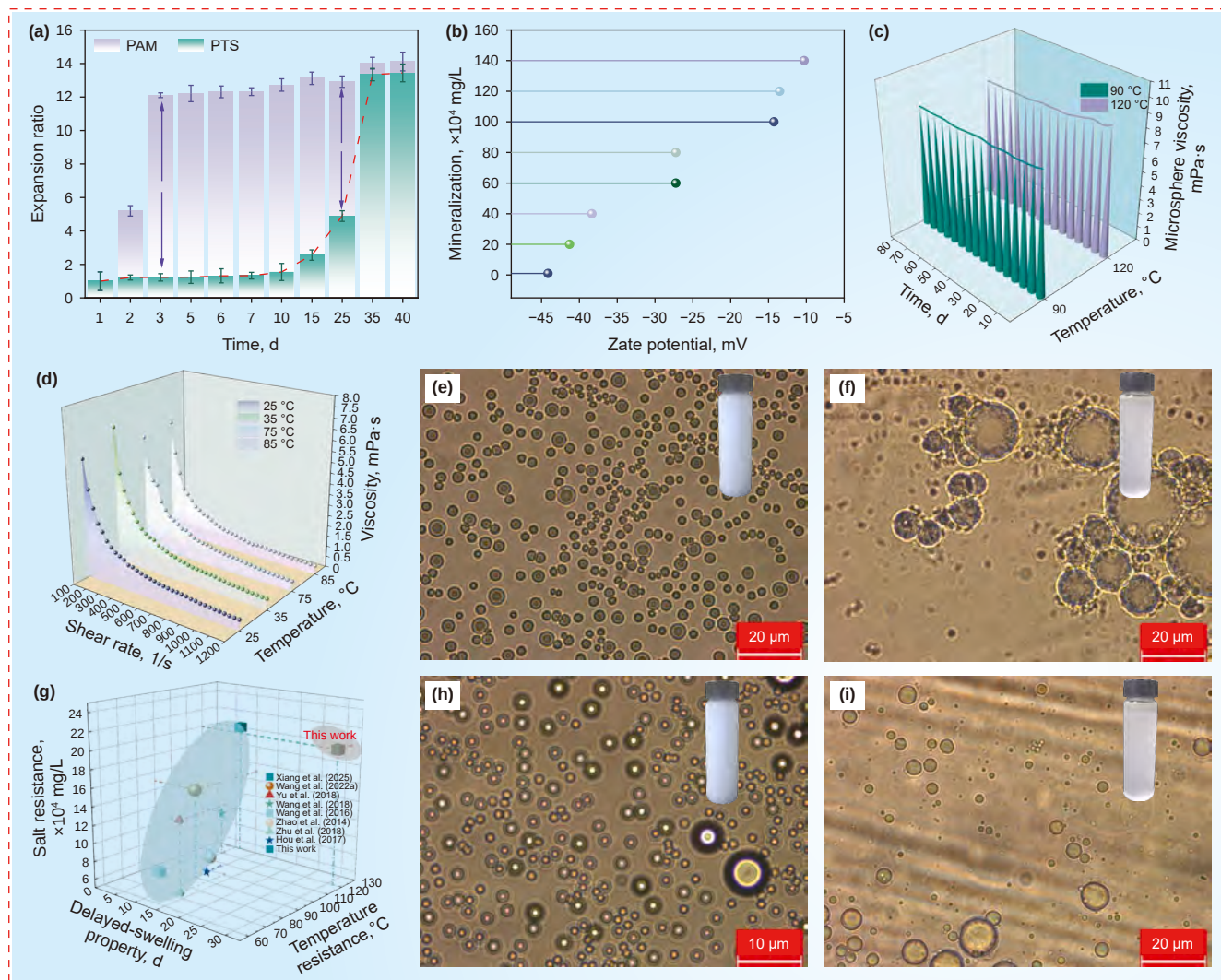


Fig. 9. (a) Swelling kinetic curve of temperature-resistant and salt-tolerant microspheres, (b) zeta potential change at different salinities, (c) aging performance of microspheres, (d) shear rheological curves at different temperatures, (e)–(j) micro-morphologies in tap water and high-salt solution (2.5×10^5 mg/L) before and after aging and (h) comparison with various literatures.

dual-network design of “chemical crosslinking-hydrophobic association” and the synergy of functional monomers, PTS microspheres achieve a unification of multiple properties including delayed swelling, salt resistance, temperature tolerance, and shear thinning, making them suitable for deep profile control in high-temperature, high-salinity reservoirs.

To further validate the technical advantages of PTS microspheres, a comparative analysis was performed between PTS and various high-performance microspheres reported in recent cutting-edge studies (Hou et al., 2017; Wang et al., 2016b; Wang et al., 2022b; Wang et al., 2018b; Xiang et al., 2025b; Yang et al., 2025; Yu et al., 2018b; Zhu et al., 2018). Fig. 9(h) displays a three-dimensional performance comparison diagram, which comprehensively evaluates the delayed swelling, temperature resistance and salt tolerance of the microspheres prepared in this study. Meanwhile, a comparative analysis was conducted with typical profile control and flooding materials reported in existing literature. It can be observed that most previously reported systems are concentrated in the light-blue region and face distinct performance limitations. For these materials, the improvement of delayed swelling behavior, thermal stability and salt tolerance is

mutually restricted, making it difficult to satisfy the harsh demands of high-temperature and high-salinity reservoirs simultaneously.

In comparison, the PTS microspheres developed in this work break through the performance envelope of conventional reported materials and achieve synchronous performance enhancement in the above three dimensions. Specifically, the product exhibits a salt tolerance higher than 20×10^4 mg/L, a thermal resistance of up to 120 °C, and remarkably superior delayed swelling capacity. This material possesses great application potential for deep profile control and flooding under severe reservoir conditions.

3.8. Evaluation of PTS for oil displacement and plugging performance

To evaluate the deep migration and plugging performance of PTS, core flooding experiments were conducted in this study. Fig. 10(a) presents a schematic diagram illustrating the profile control and water plugging mechanism of PTS in the core, while Fig. 10(b) verifies that PTS microspheres exhibit the characteristic of “delayed swelling and sustained plugging”. During the

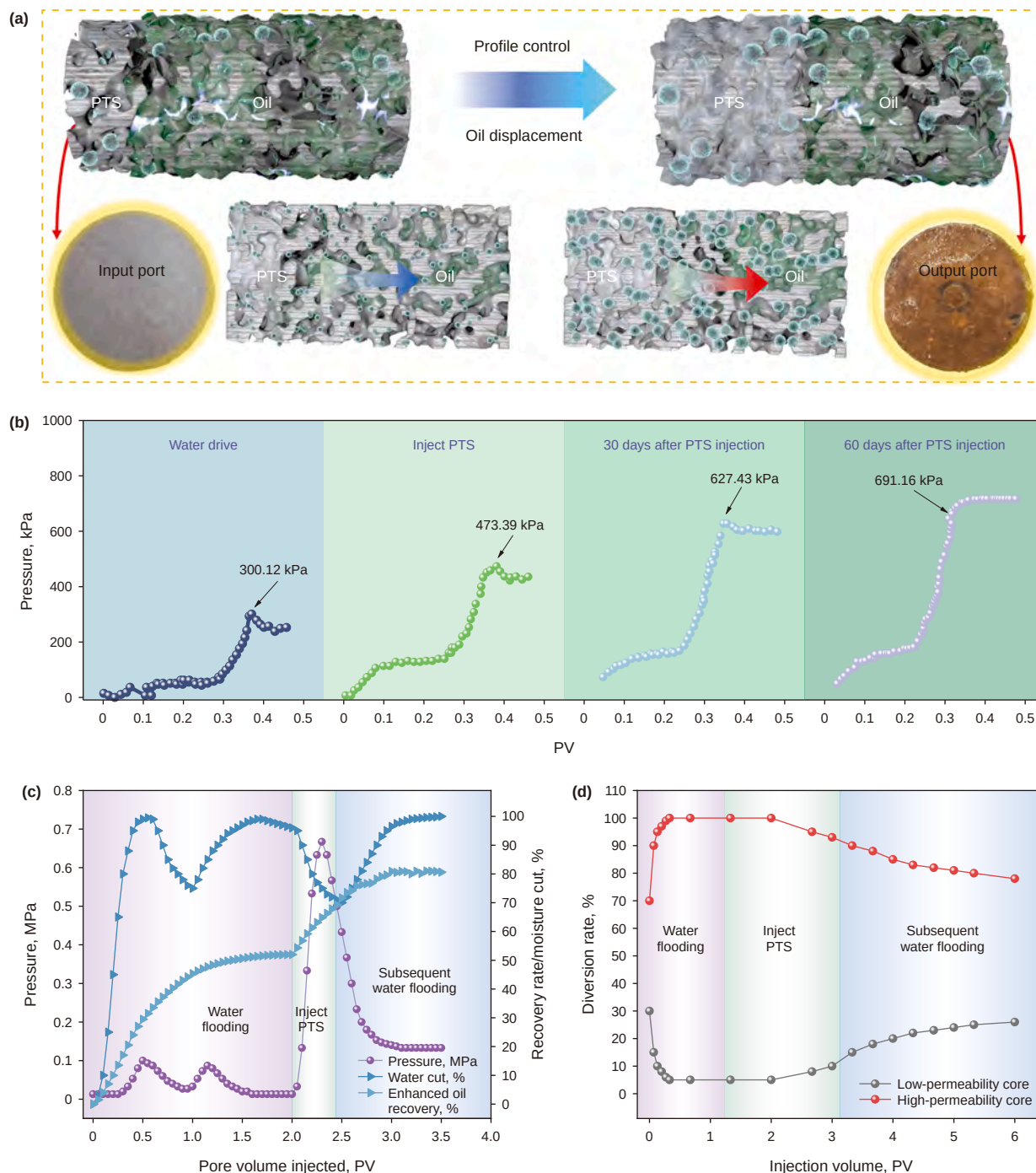


Fig. 10. Evaluation of oil displacement and plugging performance of PTS: **(a)** schematic diagram of profile control and water plugging mechanism of PTS in core, **(b)** change curve of PTS injection pressure with time (days) at 120 °C, **(c)** PTS oil displacement effect experiment, **(d)** PTS diversion efficiency.

initial water flooding stage, the injection pressure was only 300.12 kPa, and the injected water flowed freely along high-permeability channels without forming effective plugging. At the early stage of PTS injection, the pressure increased to 473.39 kPa. This phenomenon is mainly attributed to the hydrophobic microdomains formed by SMA-18 and the chemical cross-linking network constructed by the cross-linking agent DVB, which significantly hinder water molecule penetration in the initial stage. As a result, the swelling rate of the microspheres remained below 20% within 24 h, achieving only a weak occupancy effect and thus

avoiding blockage in the near-wellbore area. With the extension of PTS injection time to 30 days and 60 days, the pressure further increased to 627.43 kPa and 691.16 kPa, respectively, with a cumulative increase of 45.9% within 60 days. This observation is due to the entropy-driven dissociation of hydrophobic association sites under high-temperature conditions, allowing water molecules to gradually penetrate into the interior of the microspheres. Consequently, the microspheres slowly swell from the initial particle size of 4.02–4.57 μm to their final volume, realizing a continuously enhanced plugging effect.

The oil displacement performance of the PTS microspheres was evaluated through core flooding experiments, as illustrated in Fig. 10(c). During the primary waterflooding stage, the oil displacement efficiency stabilized at 53.1% once the water cut exceeded 98%. Subsequently, the PTS injection phase (2.0 PV) was initiated, during which the injection pressure rose significantly, indicating effective profile control and the establishment of a robust flow resistance. In the subsequent waterflooding stage, the flow paths were effectively diverted to the unwept zones, leading to a further increase in oil production. The final oil displacement efficiency reached 81.4%, representing a significant incremental oil recovery of 28.3% over conventional waterflooding. Furthermore, the water cut decreased from over 95% to below 70%, demonstrating the superior EOR potential of PTS in high-temperature and high-salinity reservoirs.

Fig. 10(d) reflects the ability of PTS microspheres in flow diversion. During the water flooding stage, the diversion rate of the high-permeability core rapidly increased to nearly 100%, while that of the low-permeability core decreased to below 5%. Fluid flow was severely concentrated in high-permeability channels, indicating poor diversion effects of traditional water flooding. In the PTS injection stage, the diversion rate of the high-permeability core slowly decreased from 100%, while the diversion rate of the low-permeability core gradually increased from below 5%. At this point, PTS microspheres occupied the high-permeability pore throats and formed initial plugging, initiating the fluid diversion process. In the subsequent water flooding stage, the diversion rate of the high-permeability core continued to decrease to 80.5%, while the diversion rate of the low-permeability core increased to more than 25.2%. This indicates that PTS microspheres achieve delayed swelling and effective plugging in high-permeability zones, driving more injected fluid into low-permeability zones and forming an efficient diversion mode of “plugging high-permeability zones and guiding fluid to low-permeability zones”. In high-permeability zones, the microspheres slowly swell to fill the pore throats, significantly increasing fluid flow resistance. In low-permeability zones, due to the limitation of pore-throat size, the microspheres only slightly swell, and their shear-thinning property ensures the smooth invasion of fluid.

Although the synthesis of O/W/O double emulsions involves a more elaborate procedure than conventional polymerization, modern high-shear continuous mixing technologies and static mixers now provide mature engineering support for the industrial scale-up of this process, ensuring the efficient production and structural stability of complex hierarchical architectures. Economically, PTS microspheres significantly increase the ultimate oil displacement efficiency from 53.1% to 81.4%, with a net gain as high as 28.3%, offering a highly compelling value proposition for the development of high-productivity ultra-deep oil reservoirs. In extreme ultra-high-temperature and high-salinity formations, conventional chemical agents typically fail due to thermal degradation or premature swelling. By contrast, with robust structural integrity and controlled swelling behavior, PTS represents a more cost-effective long-term alternative.

3.9. Molecular dynamics simulation analysis

Molecular dynamics simulations reveal distinct structural stability differences between PTS and PAM microspheres (Fig. 11(a)–(f)). The degree of polymerization ($DP = 15$) adopted in this simulation is a simplified representation of the functional segments. While this simplification may underestimate the contribution of long-range physical chain entanglement to macroscopic strength, it provides high-resolution insights into segment-level interactions and hydration behavior. Initial

conformational differences are presented in Fig. 11(a). Due to the introduction of rigid aromatic units from the DVB crosslinker and long-chain hydrophobic SMA-18 monomer, PTS molecular chains adopted a highly branched and compact conformation. In contrast, PAM existed as linear flexible chains with relatively loose molecular packing. Three-dimensional packing images showed that PTS formed a dense network structure within the simulation box, while PAM chains were dispersedly distributed with significant intermolecular voids. Dynamic conformational evolution is illustrated in Fig. 11(b) and (c). During the 0–100 ns simulation, PAM molecular chains underwent obvious disentanglement and structural collapse, with flexible segments gradually aggregating into a disordered state. In comparison, although PTS exhibited local segment separation at 80 ns, it recovered and maintained a stable spherical aggregate state at 100 ns.

Analysis of the radius of gyration (R_g) in Fig. 11(d) shows that PTS has an average R_g of 1.87 nm, much lower than the 2.31 nm of PAM, with smaller fluctuations, indicating a more stable and compact conformation. Hydrogen bond analysis in Fig. 11(e) shows that PTS has a higher hydrogen bond probability density peak at 21.37, while PAM gives a value of 17.52. PTS also has a narrower full width at half maximum and a peak at a longer bond distance. These differences arise from the synergistic effect of sulfonate groups and rigid aromatic units, which form a strong and stable hydrogen-bond network. In contrast, PAM lacks such structures and exhibits weak hydrogen bonds that can be easily disrupted. The robust hydrogen-bond network and stable hydration layer enable PTS to maintain structural integrity under high-temperature and high-salt conditions. Solvent-accessible surface area (SASA) analysis in Fig. 11(f) indicates that PTS has an average SASA of 60.5 nm², lower than the 73.9 nm² of PAM. This confirms tighter chain folding and better thermal and salt tolerance for PTS, while PAM chains are more extended and sensitive to environmental changes.

3.10. Oil displacement and plugging performance evaluation of PTS

As shown in Fig. 12(a), the profile control mechanism of PTS in the formation involves a complete process of the emulsion in rock pores: “stable emulsion migration → triggered demulsification → microsphere anchoring → delayed swelling plugging → elastic deformation and deep migration”. YH-R15 significantly reduces the oil-water interfacial tension and forms a high-strength interfacial film, maintaining the stability of the emulsion in the high-shear environment near the wellbore and avoiding blockage caused by premature release of microspheres. The oil-phase outer membrane improves the migration ability of the system in oil-bearing pores and isolates the direct erosion of high-temperature and high-salinity formation water on the microspheres. When the emulsion flows through narrow pore throats, mechanical shear or the destruction of emulsification balance triggers demulsification, and the microspheres are directionally released and anchored at the pore throats.

The released microspheres have a “chemical cross-linking—hydrophobic association” dual-network structure: the hydrophobic components inhibit the rapid penetration of water in the initial stage, achieving delayed swelling, and then gradually absorb water and swell to more than 14 times their original volume, plugging the pore throats through bridging or filling mechanisms. Under the action of displacement pressure, the elastic microspheres can deform, pass through the current plugging position, and continue to migrate deep into the formation, realizing step-by-step plugging and fluid diversion, and effectively expanding the crude oil swept volume.

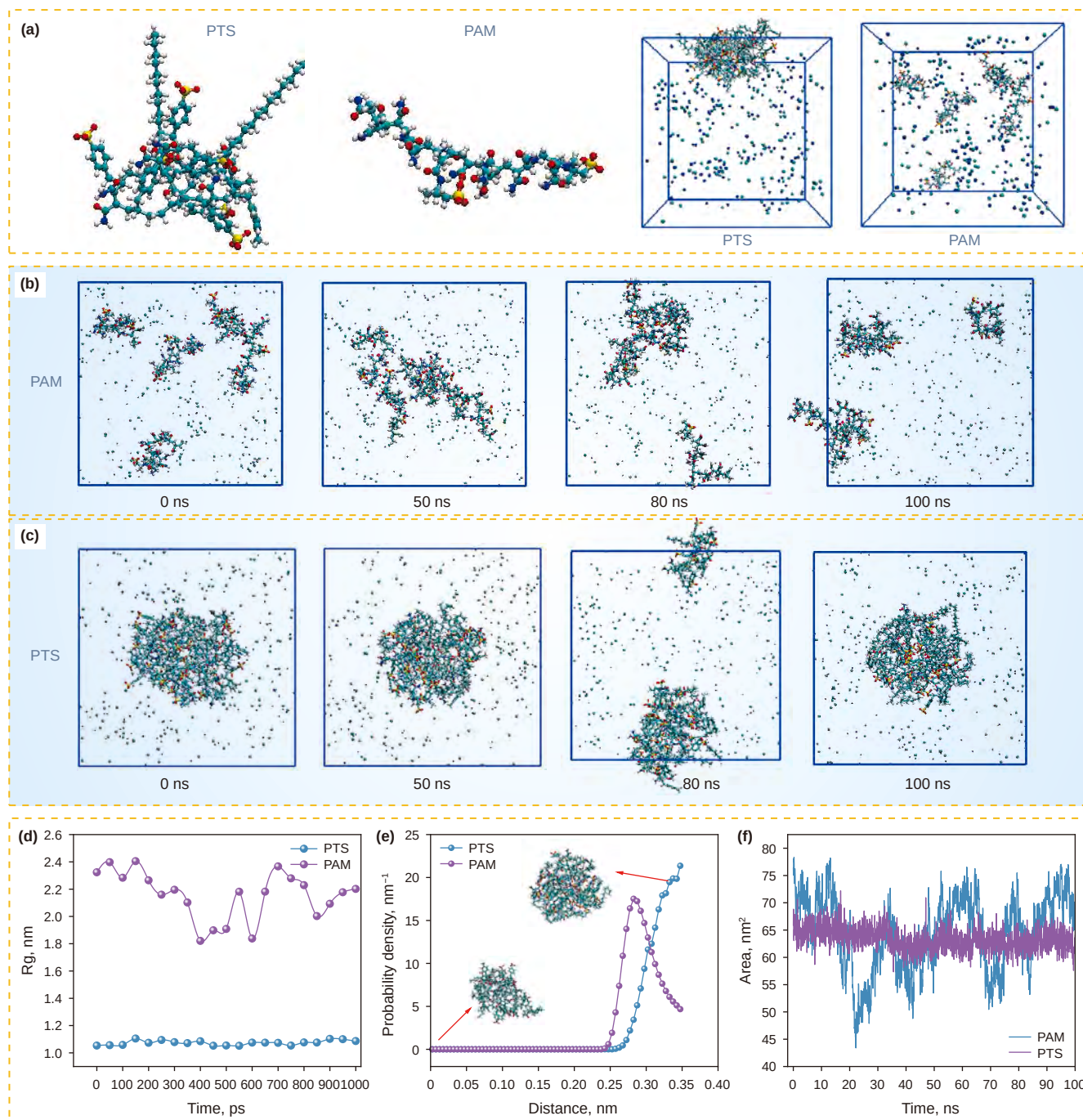


Fig. 11. Molecular dynamics simulations of PTS and PAM microspheres. **(a)** Initial molecular conformations and 3D packing of PTS and PAM, **(b–c)** conformational snapshots of PAM (b) and PTS (c) at 0, 50, 80, and 100 ns, **(d)** Time evolution of radius of gyration for PTS and PAM, **(e)** hydrogen bond distribution analysis for PTS and PAM, **(f)** time evolution of solvent-accessible surface area for PTS and PAM.

The temperature-resistant, salt-resistant, and delayed-swelling mechanisms of PTS are shown in Fig. 12(b) and (c). The dense covalent cross-linking network formed by DVB provides a rigid framework for the microspheres, and its narrow pores hinder the rapid penetration of water molecules. The SMA hydrophobic chains form dynamic physical cross-linking points, which have low affinity with water molecules and further delay the penetration of water molecules from the surface to the interior. Under high-temperature conditions, the rigid benzene ring structure of DVB inhibits the thermal movement of chain segments, and the

hydrophobic association is enhanced due to the entropy-driven effect, forming more “heat-enhanced anchor points”, which jointly maintain the network stability. The sulfonic acid groups ($-\text{SO}_3\text{H}$) exhibit excellent thermal stability and salt resistance; their high dissociation degree and strong hydration capacity effectively resist the charge shielding of high-valent ions. The “salting-out effect” caused by high salinity instead promotes hydrophobic association and enhances network rigidity.

Regarding engineering applicability, several factors should be considered for practical field deployment. First, in reservoirs with

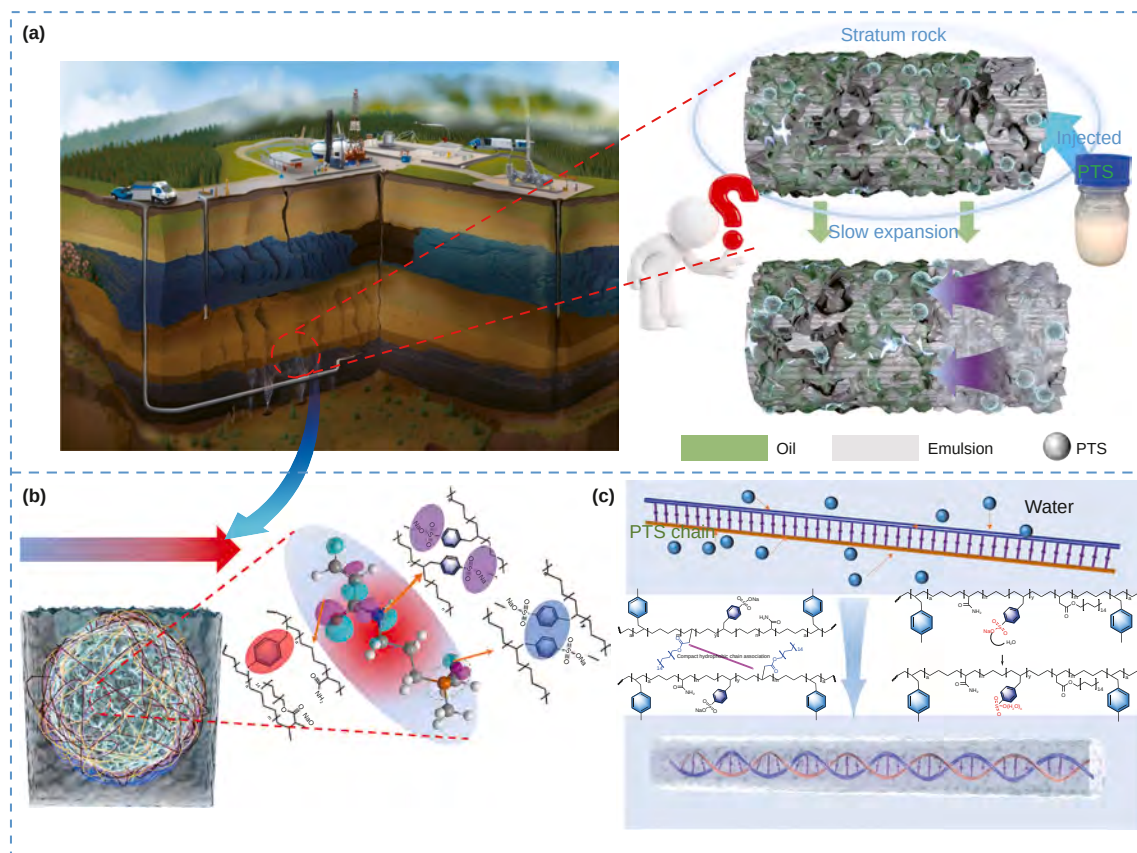


Fig. 12. (a) Schematic diagram of PTS deep profile control mechanism, (b) schematic diagram of PTS temperature resistance mechanism, (c) schematic diagram of PTS salt resistance mechanism.

different permeability contrasts, the injection concentration and particle size distribution of PTS should be optimized to match the specific pore-throat dimensions. The mean pore-throat radius of the target formation should be at least 2–3 times larger than the initial microsphere diameter ($4.02\ \mu\text{m}$) to ensure adequate injectability, while the post-swelling diameter should exceed the pore-throat size to achieve effective plugging. Based on the swelling ratio exceeding 14, PTS microspheres are suitable for formations with pore-throat radii in the range of $5\text{--}20\ \mu\text{m}$. Second, for fractured reservoirs with wide fracture apertures, PTS may be combined with larger-sized particle gels or gel systems to achieve hierarchical plugging, where PTS targets the matrix pore throats while the larger gel plugs the fractures. Third, for heterogeneous porous reservoirs with moderate permeability contrast (permeability ratio <10), PTS alone may provide sufficient profile control; however, for reservoirs with extreme heterogeneity (permeability ratio >10), a staged treatment strategy combining PTS with pre-flush or conformance control agents may be necessary.

In conclusion, through the three-dimensional synergy between chemical cross-linking, physical association, and functional groups, PTS constructs an intelligent microsphere system with delayed-swelling, temperature-resistant, and salt-resistant properties. It can adapt to the high-temperature and high-salinity reservoir environment and achieve the deep profile control goal of “injectable, migratable, and pluggable”.

3.11. Study limitations and future perspectives

While this study demonstrates the superior performance of PTS microspheres, certain limitations should be acknowledged. First,

in the molecular dynamics (MD) simulations, a simplified degree of polymerization ($DP = 15$) was selected to represent the functional segments. Although this provides high-resolution insights into segment-level interactions and hydration behavior, it may underestimate the contribution of long-range physical chain entanglements to the macroscopic mechanical strength of the microspheres. Second, the comprehensive performance comparison between PTS and other reported materials relies on data aggregated from various literatures. Due to the lack of unified benchmarks and the varying testing conditions across different studies, these comparisons are relative rather than absolute.

Future research should focus on establishing standardized evaluation protocols for ultra-high-temperature and high-salinity profile control agents to enable more rigorous cross-comparisons. Furthermore, subsequent studies will aim to scale up the double-emulsion synthesis process and transition from laboratory-scale evaluations to field pilot tests. This will be crucial for verifying the long-term plugging stability, injectivity, and flow diversion efficiency of PTS microspheres under complex, real-world reservoir conditions.

4. Conclusions

- (1) Temperature-resistant, salt-tolerant, delayed-swelling (PTS) microspheres were successfully synthesized via O/W/O double-emulsion polymerization. Stepwise emulsification constructed a spatially isolated structure with annular liquid films of $10\text{--}50\ \mu\text{m}$, providing a stable template for the dual “chemical crosslinking–hydrophobic association” network. The obtained microspheres exhibit a mean particle size of

4.02–4.57 μm , a polydispersity index of 1.013, and excellent monodisperses. The annular liquid film effectively addresses the uneven distribution of hydrophobic monomers common in traditional dispersion polymerization.

- (2) MD simulations confirm that PTS adopts a more compact molecular conformation than PAM, with an average radius of gyration of 1.87 nm, a smaller solvent-accessible surface area of 60.5 nm², and a denser hydrogen bond network with a probability density peak of 21.37. These structural features effectively prevent collapse under the high-temperature and high-salinity conditions of deep reservoirs.
- (3) PTS maintains a complete spherical structure without demulsification or precipitation after aging at 120 °C for 90 days. Across a salinity range of 0–110,000 mg L⁻¹, the zeta potential remains between -10 and -47 mV, indicating excellent colloidal stability. After 80 days of aging at 90 °C and 120 °C, the viscosity retention rate remains exceptionally high, confirming suitability for long-term application in ultra-high-temperature and high-salinity reservoirs. Following PTS treatment, the subsequent water flooding oil displacement efficiency increased to 81.4%, representing a 28.3% enhancement in oil recovery, while the water cut decreased to below 70%.
- (4) The microspheres enable efficient “block-high-and-divert-low” fluid diversion: the flow fraction of the high-permeability core decreased from nearly 100% to 80.5%, while that of the low-permeability core increased from below 5% to over 25.2%, significantly expanding the swept volume. Through synergistic mechanisms, PTS overcomes the key limitations of traditional agents—near-wellbore blockage, thermal failure, and salt intolerance—achieving deep profile control with good injectivity, deep propagation, and effective plugging in reservoirs exceeding 120 °C and 2×10^5 mg L⁻¹ salinity.

CRediT authorship contribution statement

Qiao-Lin Zuo: Writing – original draft. **Wan-Fen Pu:** Writing – review & editing. **Rui Liu:** Funding acquisition. **Shi-Tong Jiang:** Validation. **Hong-Li Liu:** Visualization.

Data availability statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of competing interest

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