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Review Article

Polyampholytes for Chemical Enhanced Oil Recovery: Recent Advances, Mechanistic Insights, and Future Perspectives

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Abstract: Chemical enhanced oil recovery (EOR) plays an important role in improving hydrocarbon production from mature reservoirs, where conventional recovery methods leave a large fraction of oil unrecovered. Among chemical EOR approaches, polymer flooding is widely used to improve mobility control and sweep efficiency. However, conventional polymers such as partially hydrolyzed polyacrylamide (HPAM) often suffer from viscosity loss, chain degradation, and poor stability under high-temperature, high-salinity, high-hardness, and high-shear reservoir conditions. This review discusses recent advances in polymer-based EOR, with particular focus on polyampholytes as next-generation mobility-control agents. Polyampholytes contain both anionic and cationic groups along the polymer backbone, enabling ionic association, salt-responsive chain conformation, and enhanced tolerance to harsh brine environments. Their antipolyelectrolyte behavior can promote chain expansion and viscosity retention at elevated salinity, distinguishing them from conventional polyelectrolytes. The review summarizes the molecular architecture, rheological behavior, reservoir interactions, and oil-displacement mechanisms of polyampholytes, including their integration with surfactants, foams, and nanoparticles. Key challenges related to synthesis, cost, injectivity, adsorption, long-term stability, and field-scale implementation are also discussed. Future perspectives emphasize the design of cost-effective, environmentally sustainable, and stimuli-responsive polyampholyte systems for demanding reservoir conditions.

Keywords: Polyampholytes; chemical enhanced oil recovery; polymer flooding; HPAM; antipolyelectrolyte effect; high-salinity reservoirs; enhanced oil recovery (EOR); sweep efficiency.

1 Introduction

The growing demand for energy and the progressive depletion of easily recoverable

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hydrocarbon reserves have intensified the need for advanced enhanced oil recovery (EOR) technologies capable of maximizing oil production from mature reservoirs. Among the various EOR approaches, polymer-based methods have attracted considerable attention because of their ability to improve sweep efficiency, regulate fluid mobility, and mitigate excessive water and gas production during reservoir operations [1]. Water-soluble polymers are particularly important owing to their relatively low cost, ease of implementation, and tunable physicochemical properties, which often provide practical advantages over alternative techniques such as foam-assisted recovery and microbial EOR processes. To address the diverse operational requirements encountered in oil reservoirs, a wide range of polymer gel systems has been developed, including bulk gels, colloidal dispersion gels, preformed particle gels, and microgels [2]. Among these materials, bulk gels represent the most extensively applied class due to their adaptability and effectiveness in conformance control applications. These systems are generally formed through the crosslinking of water-soluble polymers with suitable crosslinking agents, producing three-dimensional networks capable of modifying reservoir permeability and improving fluid distribution. Depending on their origin and chemical composition, polymers employed in EOR applications can be broadly categorized into synthetic polymers and biopolymers [3], [4].

Synthetic polymers constitute the dominant class of commercial polymer flooding agents because of their well-established production technologies and favorable rheological performance. Common examples include polyacrylamide (PAM) [5], partially hydrolyzed polyacrylamide (HPAM) [6], polyacrylamide/tert-butyl acrylate (PAtBA) copolymers [7], and acrylamide-based copolymers containing 2-acrylamido-2-methylpropane sulfonic acid (AMPS) [8]. More advanced formulations have incorporated additional functional monomers, such as N,N-dimethylacrylamide (DMA), to enhance thermal stability and salt tolerance [9], [10]. Hydrophobically associating polymers (HAPs) have also emerged as promising candidates because of their ability to generate intermolecular associations that improve viscosity retention under challenging reservoir conditions [11]. In recent years, particular attention has been directed toward amphoteric terpolymers (ATPs) composed of acrylamide (AAm), AMPS, and (3-acrylamidopropyl)trimethylammonium chloride (APTAC). These materials have demonstrated encouraging performance in high-salinity polymer flooding systems and have shown considerable potential for improving oil recovery in reservoirs where conventional polymers exhibit limited effectiveness [12], [13], [14]. Alongside synthetic materials, several naturally derived biopolymers have been investigated as environmentally benign alternatives for EOR applications. Xanthan gum [15], guar gum [16], and scleroglucan are among the most widely studied examples. Scleroglucan, in particular, has attracted significant interest because of its superior thermal stability and resistance to salinity-induced degradation compared with many conventional polyacrylamide-based systems. Current studies continue to evaluate its performance under elevated temperature conditions, high-salinity environments, and nanoparticle-assisted flooding scenarios [17]. Polyampholytes have emerged as a particularly promising class of functional polymers for addressing these challenges. These macromolecules contain both positively and negatively charged groups along the same polymer backbone, resulting in unique solution behavior that differs fundamentally from conventional polyelectrolytes [18], [97]. Owing to their responsiveness to ionic environments, polyampholytes have found applications in diverse fields including water treatment, desalination, flocculation, drilling fluids, and enhanced oil recovery [19]. Their distinctive

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molecular architecture enables them to maintain favorable rheological properties in electrolyte-rich media, making them especially attractive for applications in high-salinity reservoirs. One of the most remarkable characteristics of polyampholytes is the so-called antipolyelectrolyte effect, whereby polymer chains expand rather than contract with increasing ionic strength. Unlike traditional anionic polymers that undergo charge screening and viscosity reduction in saline environments, polyampholytes experience disruption of intramolecular electrostatic attractions, leading to chain expansion and enhanced hydrodynamic volume. This phenomenon, often referred to as a salting-in effect, results in increased solution viscosity and improved mobility control as salinity rises [20], [21]. Such behavior is highly advantageous for chemical EOR processes because it enables effective displacement performance under reservoir conditions that typically compromise the effectiveness of conventional polymer flooding agents [22], [23]. The advantages of polyampholytes become particularly evident when compared with partially hydrolyzed polyacrylamide, the most widely used commercial polymer in EOR. Although HPAM exhibits excellent thickening and viscoelastic properties in low-salinity systems, its performance deteriorates significantly in reservoirs containing high concentrations of dissolved salts [24], [25]. In contrast, zwitterionic polyampholytes have demonstrated exceptional salt tolerance and, in some cases, a pronounced increase in viscosity with increasing sodium chloride concentration. For example, acrylamide-based zwitterionic polymers containing sulfobetaine functionalities exhibit strong salt-induced thickening behavior, highlighting their potential as next-generation flooding agents for high-temperature and high-salinity reservoirs [26], [53]. These unique properties position polyampholytes as attractive alternatives to conventional EOR polymers and underscore their growing importance in the development of advanced chemical flooding technologies. To improve hydrocarbon extraction from mature reservoirs, a wide range of EOR technologies has been developed and implemented over the past several decades [27], [35]. The effectiveness of any oil recovery process is governed by two fundamental mechanisms: macroscopic displacement efficiency and microscopic displacement efficiency [28]. Macroscopic displacement efficiency, often referred to as sweep efficiency, describes the extent to which an injected fluid contacts the oil-bearing formation relative to the total reservoir volume. Microscopic displacement efficiency, on the other hand, reflects the ability of the displacing fluid to mobilize and recover oil trapped within the pore network after fluid contact has been established. Therefore, any mechanism capable of improving either volumetric sweep efficiency, pore-scale displacement efficiency, or both, contributes directly to enhanced oil recovery performance [29].

2 Overview of Enhanced Oil Recovery Methods

2.1 Classification and Chemical EOR Strategies

Among the various enhanced oil recovery (EOR) technology, chemical EOR has emerged as one of the most attractive non-thermal recovery strategies because of its relatively high recovery efficiency, economic viability, operational flexibility, and moderate capital investment requirements [27]. The widespread interest in chemical EOR intensified during the latter half of the twentieth century, driven by rising oil prices and significant advances in reservoir engineering, interfacial science, and chemical formulation technologies. Unlike conventional water flooding, chemical EOR utilizes specifically designed chemical agents to modify fluid–fluid and fluid–rock interactions within the reservoir, thereby improving oil displacement and sweep efficiency. Depending on the recovery mechanism, these chemicals can reduce the interfacial tension (IFT) between oil and water,

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increase the viscosity of the injected fluid to improve mobility control, or alter reservoir wettability to facilitate the release and transport of trapped hydrocarbons [31]. The principal chemical EOR techniques include polymer flooding, surfactant flooding, and alkaline flooding [32]. Polymer flooding primarily improves macroscopic sweep efficiency by increasing the viscosity of the injected water, thereby reducing the mobility ratio between the displacing and displaced phases. Surfactant flooding enhances microscopic displacement efficiency through substantial reductions in oil–water interfacial tension, enabling the mobilization of capillary-trapped oil [30]. Alkaline flooding operates through the in situ generation of surface-active species resulting from reactions between alkaline agents and acidic components of crude oil, leading to reduced interfacial tension and improved oil recovery [33], [34]. Despite their demonstrated effectiveness, these conventional chemical flooding approaches face several technical challenges under harsh reservoir conditions. Polymer solutions often experience thermal degradation, mechanical degradation, and salinity-induced viscosity loss, particularly in reservoirs characterized by elevated temperatures and high concentrations of dissolved salts [25]. Similarly, surfactants and alkaline agents frequently suffer from adsorption onto reservoir rock surfaces, reducing their effective concentration and limiting their displacement performance within porous media [36]. These limitations have motivated the development of more sophisticated chemical flooding formulations designed to exploit synergistic interactions among multiple chemical agents [37]. To overcome the shortcomings associated with individual flooding agents, several hybrid chemical EOR strategies have been developed, including alkaline–surfactant (AS), surfactant–polymer (SP), alkaline–polymer (AP), and alkaline–surfactant–polymer (ASP) flooding systems [38] (Figure 1). These integrated formulations combine the advantages of their constituent chemicals, resulting in improved mobility control, lower interfacial tension, enhanced sweep efficiency, and greater overall oil recovery. Numerous laboratory investigations and field applications have demonstrated that these hybrid approaches generally outperform single-component flooding systems owing to their complementary recovery mechanisms [39], [40].

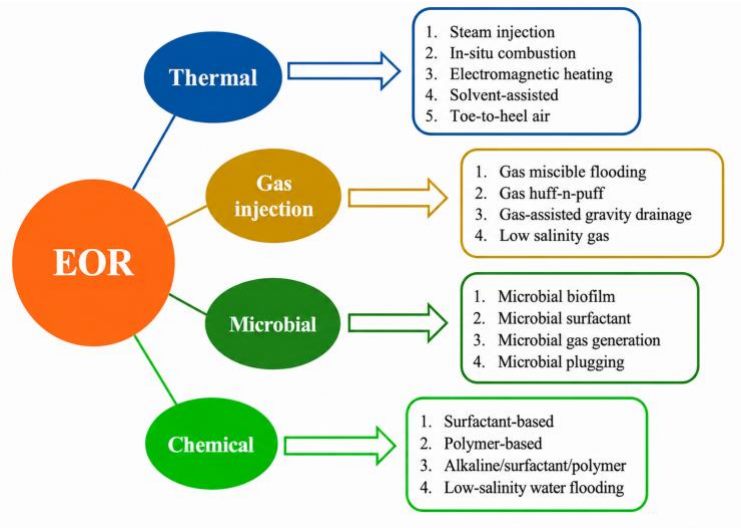

Figure 1. Simplified classification of EOR methods.

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More recently, increasing attention has been directed toward foam-assisted chemical EOR processes [41], [42], [43]. The incorporation of polymers and surfactants into foam formulations has been shown to improve foam stability, reduce gas mobility, and enhance conformance control within heterogeneous reservoirs. Such systems can effectively divert injected fluids into previously inswept regions of the reservoir, thereby increasing volumetric sweep efficiency and improving hydrocarbon recovery. These advances highlight the ongoing evolution of chemical EOR technologies and underscore the importance of developing robust, salt-tolerant, and thermally stable chemical systems capable of maintaining high performance under increasingly challenging reservoir conditions.

2.2 Role of Nanotechnology in Chemical EOR

Recent advances in nanoscience and nanotechnology have transformed numerous industrial sectors, including metallurgy, electronics, medicine, catalysis, aerospace engineering, and energy conversion systems. These developments have also stimulated growing interest in the application of nanotechnology within the petroleum industry, particularly for addressing challenges associated with oil recovery and reservoir management. Nanotechnology generally involves the design, synthesis, and utilization of materials possessing at least one dimension within the nanoscale range of approximately 1–100 nm. Such engineered nanomaterials, commonly referred to as nanoparticles, exhibit unique physicochemical properties arising from their high surface-area-to-volume ratios and size-dependent quantum effects. When dispersed within a suitable carrier medium such as water, oil, or gas, these nanoparticles form nanofluids capable of delivering enhanced functional performance compared with conventional fluids. Consequently, nanotechnology has been explored for a broad range of upstream oil and gas applications, including drilling operations, petroleum exploration, mitigation of asphaltene deposition, inhibition of gas hydrate formation, hydraulic fracturing, and enhanced oil recovery (EOR) [42], [43].

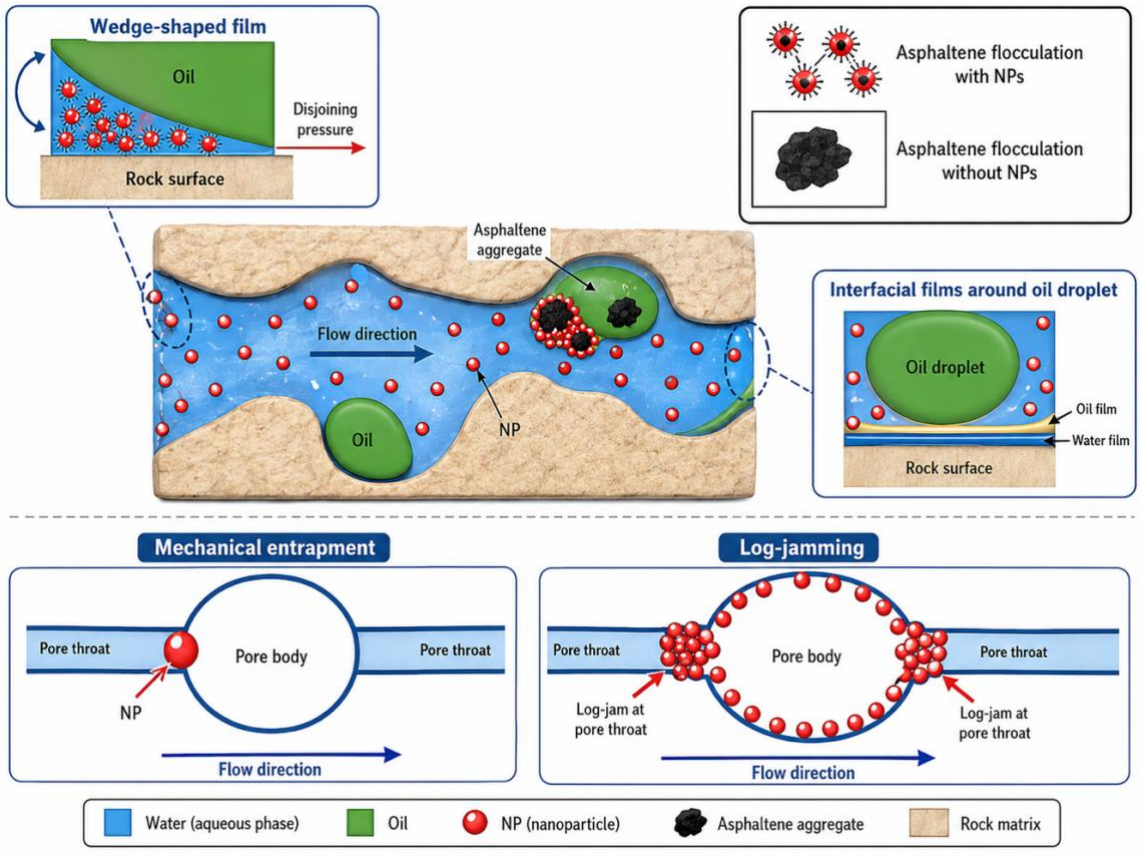

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Figure 2. Schematic illustration of the principal mechanisms governing nanotechnology-assisted enhanced oil recovery [adapted from 57].

As presented in Figure 2, the effectiveness of nanoparticle-assisted EOR has been attributed to several complementary mechanisms, including structural disjoining pressure, wettability modification, interfacial tension (IFT) reduction, and enhancement of injected-fluid rheological properties [42], [43]. More recently, nanoparticles have been incorporated into conventional EOR formulations to create hybrid systems with improved physicochemical performance. For example, polymer-based nanofluids have demonstrated superior rheological stability, enhanced viscosity retention, and improved resistance to harsh reservoir conditions characterized by elevated temperatures and high salinity [44]. Similarly, the incorporation of nanoparticles into surfactant systems has been shown to reduce surfactant adsorption onto reservoir rock surfaces through competitive adsorption mechanisms, thereby improving chemical utilization efficiency [45]. In foam-based EOR processes, nanoparticles can enhance foam stability and extend foam half-life, resulting in improved mobility control and sweep efficiency [65], [67], [68]. The most widely applied chemical EOR agents remain polymers, surfactants, and alkaline chemicals. Polymer flooding improves recovery efficiency primarily by increasing the viscosity of the injected aqueous phase, thereby reducing the mobility ratio between water and oil and improving sweep efficiency throughout the reservoir. In addition, polymer solutions can decrease the effective permeability to water, further enhancing displacement performance and hydrocarbon recovery [49]. Surfactant flooding operates through the reduction of oil–water interfacial tension by promoting the formation of interfacially active species and facilitating emulsification processes. The resulting decrease in capillary forces enables the mobilization of trapped and residual oil, while surfactant adsorption can simultaneously alter reservoir wettability to favor oil displacement.

Alkaline flooding functions through similar mechanisms, generating surface-active compounds in situ through reactions between alkaline agents and acidic components of crude oil, thereby contributing to interfacial tension reduction and improved recovery [50]. Foam flooding, on the other hand, improves conformance control by diverting injected fluids from high-permeability thief zones toward previously unswept, low-permeability regions of the reservoir, ultimately increasing volumetric sweep efficiency. To maximize the benefits of individual chemical flooding techniques, several integrated EOR approaches have been developed, including alkaline–polymer (AP), alkaline–surfactant (AS), surfactant–polymer (SP), and alkaline–surfactant–polymer (ASP) flooding systems. These hybrid formulations combine the complementary advantages of their constituent chemicals, leading to simultaneous improvements in mobility control, interfacial properties, wettability modification, and sweep efficiency. As a result, AP, AS, SP, and ASP flooding technologies have demonstrated significant potential for increasing the recovery of original oil in place (OOIP) beyond the limits achievable by single-component flooding processes.

3 Polymer Flooding Technology

Polymer flooding is one of the most widely implemented chemical enhanced oil recovery (EOR) techniques and involves the addition of water-soluble polymers to the injection water to improve reservoir sweep efficiency. The primary objective of polymer flooding is to increase the viscosity of the injected aqueous phase, thereby reducing the mobility ratio between the displacing water and the displaced oil. A more favorable mobility ratio suppresses viscous fingering and channeling phenomena, enabling a more uniform displacement front and improved volumetric sweep efficiency throughout the reservoir [46]. Consequently, polymer flooding has proven

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particularly effective in heterogeneous formations and heavy-oil reservoirs and has been successfully applied in both sandstone and carbonate reservoirs worldwide [48]. The transport behavior of polymer solutions in porous media is considerably more complex than that of conventional Newtonian fluids. Most polymers used in EOR exhibit non-Newtonian rheological behavior, and their flow characteristics within reservoir rocks are influenced by factors such as viscoelasticity, shear rate, pore structure, and inaccessible pore volume (IAPV). Although the rheological properties of polymer solutions are commonly measured under bulk conditions using rheometers, their apparent viscosity during flow through porous media often differs substantially from the measured bulk viscosity [49], [60]. Flexible polymers such as partially hydrolyzed polyacrylamide (HPAM) typically exhibit a sequence of rheological responses during flow through porous structures, including Newtonian behavior at low shear rates, shear-thinning at intermediate shear rates, viscoelastic shear-thickening at elevated shear rates, and eventual shear-thinning caused by mechanical degradation under extreme flow conditions [62]. The determination of inaccessible pore volume remains an important aspect of polymer flooding studies because it influences polymer transport and retention within reservoir rocks. Conventionally, IAPV is evaluated through core-flooding experiments using polymer solutions in conjunction with inert tracers. The breakthrough behavior of both the polymer and tracer is subsequently analyzed to estimate the fraction of pore space inaccessible to polymer molecules. However, accurate quantification often requires sophisticated analytical methods and instrumentation, and the presence of crude oil can further complicate concentration measurements and data interpretation [56]. Despite decades of waterflooding operations, a substantial proportion of the original oil in place remains unrecovered in many reservoirs, particularly those characterized by pronounced heterogeneity. Once preferential flow channels develop between injection and production wells, subsequently injected water tends to follow these low-resistance pathways, bypassing significant portions of the oil-bearing formation. This phenomenon results in poor sweep efficiency, early water breakthrough, and reduced oil recovery. Polymer flooding addresses this limitation by increasing the viscosity of the injected water, thereby improving mobility control and promoting a more uniform displacement of hydrocarbons across the reservoir. As a result, polymer flooding can substantially enhance volumetric sweep efficiency and recover oil that would otherwise remain bypassed during conventional waterflooding operations [46], [50]. The commercial success of polymer flooding has established it as one of the most effective and economically viable EOR technologies. Large-scale field implementations have demonstrated its capacity to generate substantial incremental oil production, with the Daqing Oilfield in China representing one of the most notable examples, where polymer flooding contributed significantly to enhanced hydrocarbon recovery and sustained field productivity [54], [55]. Similar successes have been reported in major reservoirs located in Canada, Oman, and Suriname, highlighting the broad applicability of this technology under diverse geological and operational conditions [59].

The effectiveness of any displacement process is governed by both macroscopic and microscopic recovery efficiencies. Macroscopic recovery efficiency is associated with the volume of reservoir contacted by the injected fluid, whereas microscopic recovery efficiency reflects the ability of the displacing fluid to mobilize oil trapped within pore spaces by capillary forces. Improvements in either mechanism contribute directly to increased hydrocarbon recovery [60]. However, studies have demonstrated that substantial improvements in microscopic displacement efficiency generally require significant increases in capillary number. This realization has motivated extensive investigations into the mechanisms responsible for enhanced recovery during polymer flooding and has stimulated the development of advanced polymer systems with improved performance characteristics.

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Among commercially available EOR polymers, HPAM remains the most widely utilized owing to its low production cost, availability at industrial scale, and tunable physicochemical properties, including molecular weight and degree of hydrolysis [61]. Nevertheless, conventional polyacrylamide-based polymers exhibit several limitations under harsh reservoir conditions. Their performance can be adversely affected by thermal degradation, mechanical degradation, chemical instability, and microbial attack. These challenges become particularly pronounced in reservoirs characterized by elevated temperatures, high salinity, and high concentrations of divalent ions, where polymer effectiveness may decline significantly. Consequently, considerable research efforts have focused on developing alternative polymer systems with enhanced thermal stability and salt tolerance, including hydrophobically modified polymers, biopolymers, and amphoteric polymer formulations [62]. Water remains the most common displacing fluid in oil production operations; however, unfavorable viscosity contrasts between water and crude oil often lead to unstable displacement fronts and poor sweep efficiency, particularly in heterogeneous formations. The incorporation of water-soluble polymers into injection brines improves the rheological properties of the displacing phase and has therefore become a widely adopted strategy in many oilfields. The performance of these polymers under saline conditions is particularly important because reservoir brines frequently contain substantial concentrations of dissolved salts. Beyond EOR applications, polyacrylamide-based materials have found extensive use in wastewater treatment, paper manufacturing, and numerous industrial processes due to their excellent thickening, flocculation, and rheological properties

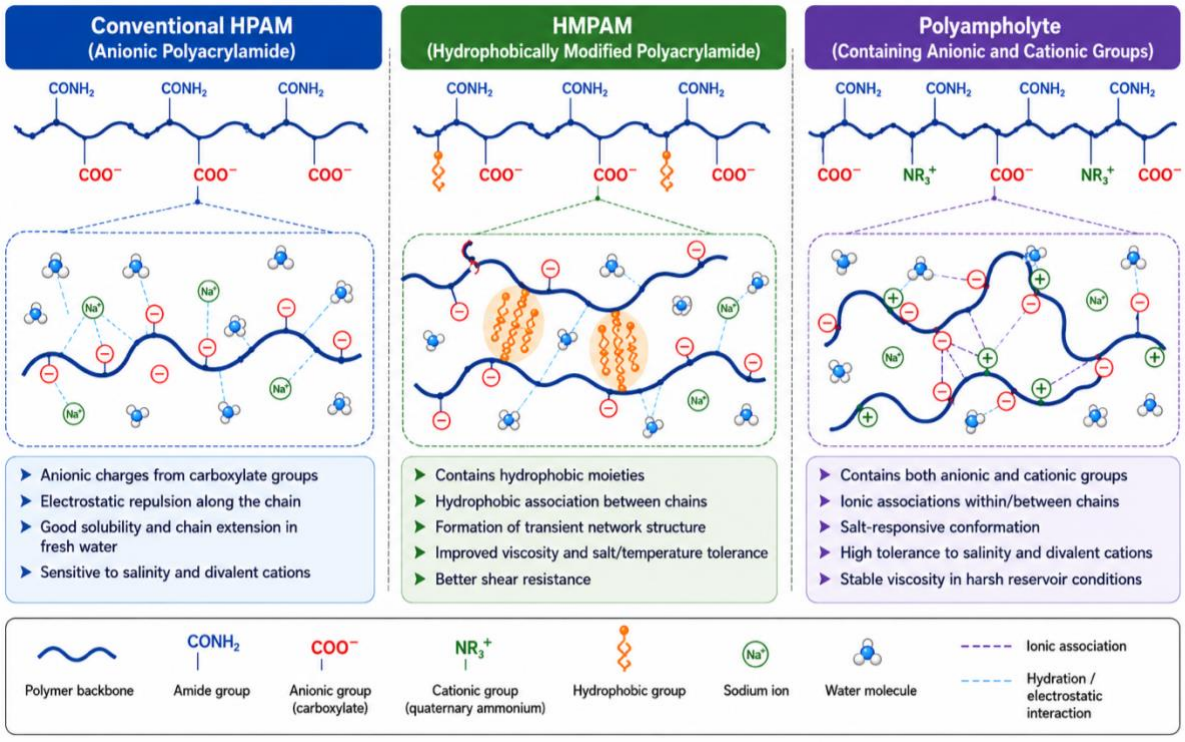

Fig. 3. Molecular architecture and interaction mechanisms of representative polymers used in chemical enhanced oil recovery (EOR).

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Conventional HPAM contains amide and anionic carboxylate groups, HMPAM incorporates hydrophobic moieties that promote associative network formation, and polyampholytes contain both anionic and cationic groups that enable ionic association and salt-responsive conformational behavior. The schematic was created by the authors based on the general molecular features of EOR polymers (Figure 3). The viscosity-enhancing capability of HPAM originates from electrostatic repulsion between negatively charged groups distributed along the polymer backbone, which promotes chain expansion and increases hydrodynamic volume in solution. However, the presence of dissolved salts can screen these electrostatic interactions, causing polymer chains to contract and reducing solution viscosity. Consequently, higher polymer concentrations are often required to achieve target viscosities in saline environments. Under extreme salinity and temperature conditions, polymer chains may undergo severe contraction, aggregation, and precipitation, resulting in substantial performance losses. These limitations have driven the search for more robust polymer architectures capable of maintaining favorable rheological properties under challenging reservoir conditions.

In practical applications, polymer flooding involves the injection of high-molecular-weight water-soluble polymers together with the waterflood to improve mobility control and conformance throughout the reservoir [63]. By increasing the viscosity of the injected phase, polymers reduce the tendency for viscous fingering and promote a more stable displacement front. The resulting improvement in sweep efficiency enables the recovery of additional hydrocarbons from regions that would otherwise remain unswept. These advantages have established polymer flooding as a cornerstone of modern chemical EOR and continue to drive the development of next-generation polymer systems designed for increasingly demanding reservoir environments.

3.1 Mobility Ratio and Sweep Efficiency

$$M = \frac{(K_w/\mu_w)}{(K_o/\mu_o)} \quad (1)$$

In the mobility ratio expression, *M* represents the mobility ratio, *Kw* and *Ko* denote the effective permeabilities of water and oil, respectively, while *μw* and *μo* correspond to the viscosities of water and oil. A favourable mobility ratio is essential for achieving efficient displacement and maximizing reservoir sweep efficiency.

The mobility ratio (**M**) (equation 1) is one of the most important parameters in enhanced oil recovery (EOR) because it describes the relative ease with which the displacing fluid moves compared with the displaced oil. It is defined as the ratio of water mobility to oil mobility and is governed by the effective permeabilities and viscosities of both phases. A favorable mobility ratio (**M ≤ 1**) promotes a stable displacement front, improves sweep efficiency, and reduces viscous fingering and channeling, whereas an unfavorable mobility ratio (**M > 1**) can lead to poor sweep efficiency and early breakthrough of the injected fluid. Therefore, polymer flooding aims to increase the viscosity of the injected water, thereby reducing the mobility ratio and enhancing oil recovery efficiency [46], [49], [60].

Among the parameters influencing mobility control, increasing the viscosity of the injected water represents the most practical and economically viable approach. This objective can be readily achieved through the incorporation of high-molecular-weight water-soluble polymers into the injection fluid. The resulting increase in aqueous-phase viscosity improves the mobility ratio between water and oil, thereby enhancing displacement efficiency and reducing the tendency of injected water to bypass oil-bearing regions. Consequently, the propagation velocity of the injected water decreases relative to that of the displaced oil, allowing a larger reservoir volume to be contacted and contributing to increased hydrocarbon production [46], [50]. Numerous laboratory investigations and field applications have demonstrated that polymer flooding is particularly

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effective for the recovery of viscous crude oils and for improving the productivity of mature reservoirs [46], [50]. In addition to mobility control, polymer viscoelasticity has been recognized as another important mechanism contributing to enhanced oil recovery and improved macroscopic sweep efficiency (Figure 4). Unlike Newtonian fluids, polymer solutions exhibit complex viscoelastic behavior when flowing through porous media. As polymer molecules migrate through pore networks, they continuously undergo deformation, extension, and relaxation processes in response to variations in pore geometry and flow conditions [49], [60]. These dynamic molecular interactions generate elastic forces that can improve the displacement of trapped hydrocarbons, stabilize the advancing flood front, and enhance the overall efficiency of the recovery process. Consequently, the viscoelastic properties of polymer solutions are increasingly regarded as a critical factor governing the success of modern polymer flooding operations, particularly in heterogeneous reservoirs where conventional waterflooding often performs poorly.

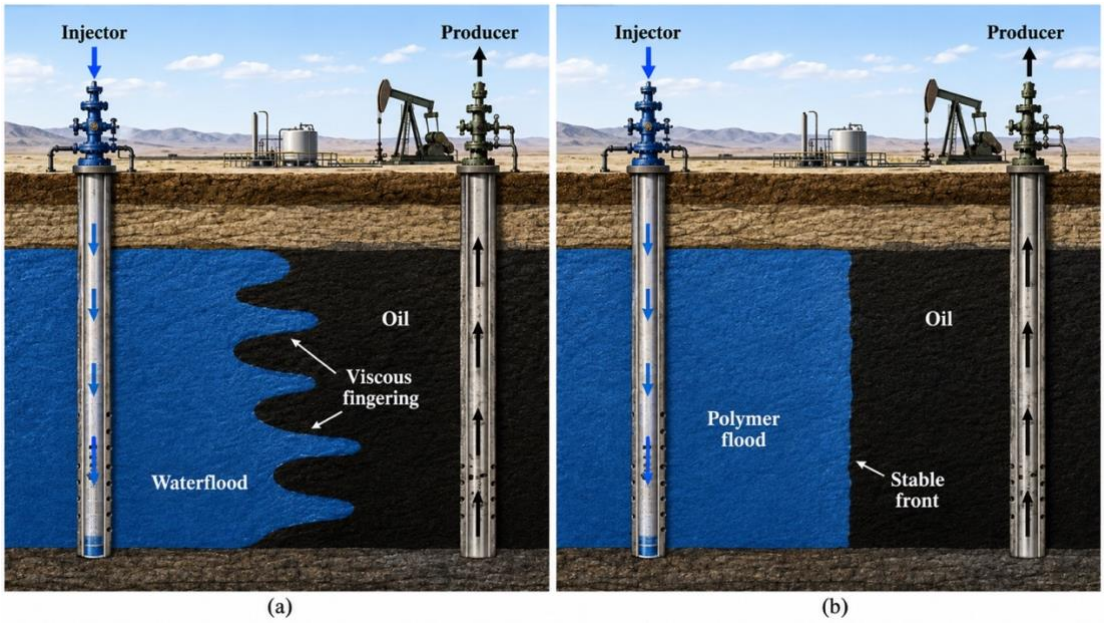

Figure 4. Typical mobility ratio of (a) water flooding process (M > 1.0), (b) polymer flooding process (M ≤ 1.0).

Schematic created by the authors based on concepts reported in Refs. [46], [49], [60].

3.2 Viscoelasticity and Flow Through Porous Media

The viscoelastic nature of polymer solutions contributes significantly to both macroscopic and microscopic displacement efficiencies by generating an additional elastic component during flow through porous media. This elastic behavior enhances the interaction between the displacing fluid and trapped oil, leading to improved sweep performance and more effective mobilization of residual hydrocarbons. Several studies have investigated the influence of polymer viscoelasticity on oil recovery performance and sweep efficiency. In these investigations, polymer solutions possessing similar shear viscosities but differing molecular weight distributions were employed to isolate the effect of elasticity on displacement behavior. The experimental results demonstrated that polymer solutions with higher elastic properties exhibited greater resistance to flow through porous media and produced a more stable displacement front. The enhanced front stability reduced the development of viscous fingering and channeling phenomena, resulting in a more uniform sweep of the reservoir volume. Consequently, reservoirs flooded with highly elastic polymer solutions displayed improved volumetric sweep efficiency, reduced residual oil saturation, and enhanced overall oil recovery compared with systems exhibiting lower elastic

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responses. These findings highlight the critical role of polymer viscoelasticity in determining flooding performance and further support the development of advanced polymer formulations capable of maintaining favorable rheological and elastic properties under reservoir conditions.

Table 1. Classification and performance comparison of polymers commonly applied in EOR. Summarized based on Refs. [50], [52], [56]–[58], [63].

Polymer type	**Polymer class**	**Main strengths for EOR**	**Main limitations**	**Suitable reservoir conditions**
HPAM	Synthetic polymer	High water solubility; good viscosity enhancement; widely used in field applications; relatively low cost	Sensitive to high temperature, salinity, divalent cations, and mechanical degradation	Low-to-moderate salinity reservoirs with controlled temperature conditions
HAPAM	Modified synthetic polymer	Improved thickening behavior; lower retention in porous media; better tolerance than conventional HPAM in some brines	Performance depends strongly on polymer concentration, salinity, and molecular structure	Reservoirs requiring improved mobility control and moderate salinity tolerance
Xanthan gum	Biopolymer	Good thermal stability; relatively good shear resistance; tolerant to salinity and hardness	Susceptible to microbial degradation; may increase plugging risk in porous media	Reservoirs where biological stability can be controlled and injectivity is acceptable
Welan gum	Biopolymer	Good long-term viscosity stability; favorable viscoelastic behavior; better thermal tolerance than some natural polymers	May interact with inorganic cations in reservoir brines	Reservoirs with moderate-to-high temperature where viscosity stability is important
Guar gum	Natural polymer	Environmentally friendly; good hydration behavior; compatible with aqueous systems	Temperature-sensitive; may degrade under harsh reservoir conditions	Mild reservoir conditions and applications where biodegradability is preferred
Cellulose	Natural polymer	Resistant to mechanical shear; can show temperature resistance after modification	Poor water solubility; heterogeneous swelling may affect injectivity	Mainly useful after chemical modification rather than in native form
Carboxymethylcellulose	Cellulose derivative	Environmentally friendly; moderate water solubility; useful viscosifying behavior	Thermal degradation and oxidative decomposition may occur	Moderate-temperature reservoirs and environmentally oriented EOR formulations
Hydroxyethylcellulose	Cellulose derivative	High water solubility; good viscosifying effect; resistant to shear and moderate temperature	Biodegradation risk under uncontrolled microbial conditions	Reservoirs where water-soluble cellulose derivatives are preferred

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4 Types of Polymers for Polymer Flooding

Polymers employed in polymer flooding operations are broadly classified into two major categories: synthetic polymers and biopolymers [50], [52]. These materials differ significantly in their chemical structures, physicochemical properties, environmental compatibility, and performance under reservoir conditions. The selection of an appropriate polymer depends on several factors, including reservoir temperature, salinity, permeability, crude oil characteristics, and economic considerations. Synthetic polymers currently dominate commercial polymer flooding applications owing to their availability, relatively low production cost, and tunable molecular architectures. The most extensively used materials include polyacrylamide-based polymers and their derivatives, such as partially hydrolyzed polyacrylamide (HPAM), hydrophobically associating polyacrylamide (HAPAM), and various acrylamide-based copolymers specifically designed to improve thermal stability, salinity tolerance, and rheological performance. These polymers can be engineered to achieve desirable molecular weights, charge densities, and functional group compositions, enabling their adaptation to a wide range of reservoir environments. Biopolymers represent a renewable and environmentally friendly alternative to synthetic polymers and have attracted increasing attention in recent years. HPAM continues to be the industry benchmark because of its cost-effectiveness and proven performance, whereas xanthan gum and other biopolymers are valued for their viscosity retention and tolerance to adverse reservoir environments [57]. Owing to their widespread commercial application and extensive research history, these two polymers have served as reference materials for evaluating the performance of newly developed flooding agents. Recent advances in polymer science have also stimulated interest in biopolymer-derived materials, particularly polysaccharides and polypeptides, as sustainable alternatives for chemical EOR. Comprehensive reviews detailing the development, properties, and performance of these emerging materials have been reported elsewhere [52], [63]. A comparative summary of the advantages and limitations of synthetic polymers and biopolymers used in EOR applications is presented in Table 1.

5 Hybrid Polymer-Based Chemical EOR Systems

5.1 Polymer–Foam Flooding

Polymer–foam flooding has emerged as a promising hybrid enhanced oil recovery (EOR) technology that combines the favorable mobility-control characteristics of polymer flooding with the superior conformance-control capabilities of foam systems. In these formulations, polymers are incorporated into foam structures to improve foam stability and enhance displacement efficiency under reservoir conditions. Owing to their high molecular weight, viscoelastic behavior, and ability to modify solution rheology, polymers can significantly improve foam performance even at relatively low concentrations, making polymer–foam flooding both technically attractive and economically feasible. The addition of polymers increases the viscosity of the liquid phase within the foam structure, thereby reducing liquid drainage from foam lamellae and enhancing foam stability. This improved stability prolongs foam persistence within porous media and enhances its ability to regulate fluid mobility. As a result, polymer-stabilized foams exhibit superior resistance to coalescence and collapse, enabling more effective blockage of high-permeability flow channels and improving sweep efficiency throughout the reservoir. These characteristics make polymer–foam systems particularly effective for controlling gas mobility and mitigating the adverse effects of reservoir heterogeneity during oil recovery operations. In

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addition to directly stabilizing foam films, polymers are frequently employed as auxiliary components in surfactant-stabilized and nanoparticle-stabilized foam systems. In such hybrid formulations, polymers help maintain the adsorption of surfactant molecules and nanoparticles at the gas–liquid interface, thereby preventing their detachment from foam lamellae. This enhanced interfacial stabilization reduces foam coalescence, increases foam half-life, and improves overall foam durability under harsh reservoir conditions (Figure 5). Consequently, polymer–foam flooding has attracted considerable attention as an advanced EOR strategy capable of delivering improved mobility control, enhanced sweep efficiency, and increased hydrocarbon recovery compared with conventional foam flooding systems.

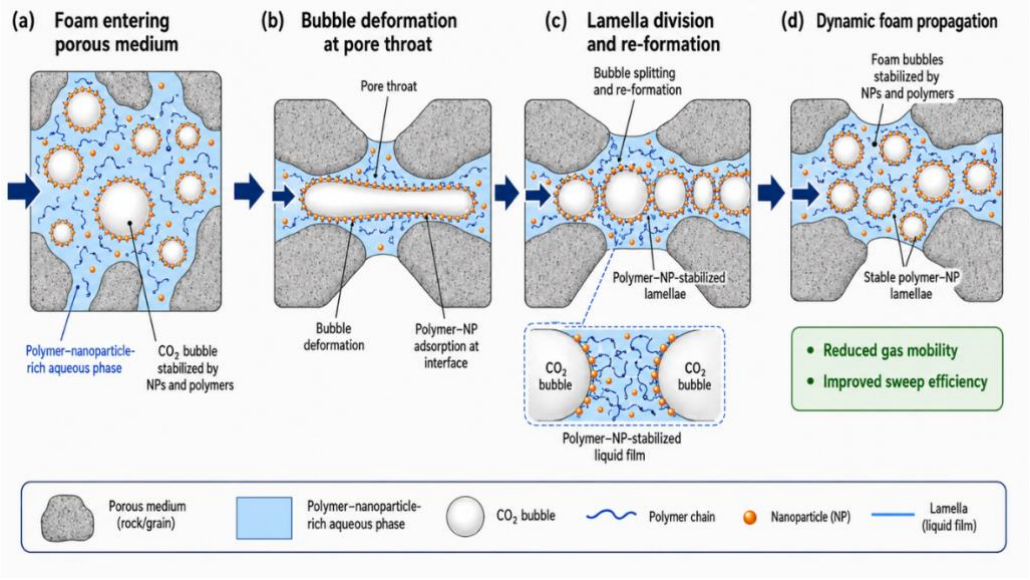

Figure 5. Schematics of polymer-stabilized nanoparticle foam. Created by the authors based on concepts reported in Refs. [64], [65], [66], [67], [68].

Both synthetic polymers and biopolymers have demonstrated significant potential as foam stabilizing agents in enhanced oil recovery applications. Their effectiveness is primarily attributed to their ability to increase the viscosity of the continuous phase, strengthen foam films, suppress liquid drainage, and improve foam durability under reservoir conditions. These characteristics enable polymer-enhanced foams to provide superior mobility control and conformance improvement compared with conventional foam systems. Several studies have highlighted the influence of polymer structure on foam performance. The advantages of associative polymers have also been demonstrated in comparative studies. Ahmed et al. [64] reported that a novel associative polymer generated significantly stronger foams than HPAM under similar conditions. The resulting foam exhibited approximately twice the apparent viscosity of HPAM-stabilized systems, reflecting improved rheological behavior and enhanced tolerance to adverse reservoir environments. In contrast, AOS foams prepared without polymer additives experienced rapid liquid drainage and accelerated collapse. Consequently, associative polymer-stabilized foams achieved an incremental oil recovery of 28%, compared with only 14% obtained using polymer-free foams. These findings indicate that the incorporation of hydrophobic functionalities into polymer structures can substantially improve foam stability and displacement performance.

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Recent research has increasingly focused on hybrid nanoparticle–polymer foam systems designed for harsh reservoir conditions. Bashir et al. [65] investigated the stability and rheological properties of CO_2 foams stabilized by nanoparticles and xanthan gum under high-temperature and high-salinity conditions in the presence of oil. Using fumed silica nanoparticles and rice husk ash as nanoparticle additives, the authors observed that foam stability improved with increasing polymer molecular weight and decreasing nanoparticle size. The enhanced performance was attributed to the synergistic action of polymers and nanoparticles, which promoted the formation of stable emulsified oil droplets capable of traversing foam lamellae without destabilizing the surfactant film. Biopolymer-based foam stabilizers have also attracted considerable attention. Wei et al. [66] examined the combined effect of xanthan gum and alkyl polyglycoside (APG) surfactants on foam stability in oil-containing systems. The presence of xanthan gum significantly increased the viscosity of the liquid film and improved foam stability through multiple mechanisms. First, the polysaccharide enhanced interfacial elasticity and facilitated the formation of dense adsorption layers at the gas–liquid interface. Second, these interactions promoted the formation of stable pseudo-emulsion films capable of resisting rupture in the presence of oil. Finally, the increased liquid viscosity reduced drainage rates and improved emulsion stability, thereby extending foam lifetime. The stabilization potential of cellulose-derived materials has likewise been demonstrated. Wei et al. [67] reported that surface-grafted nanocellulose effectively suppressed liquid drainage and increased foam film thickness, leading to improved foam durability. The performance of polymer-stabilized foams is influenced not only by polymer composition but also by reservoir conditions and fluid properties. Parameters such as crude oil viscosity, salinity, and temperature can significantly affect foam stability and effectiveness. Generally, highly viscous oils promote foam destabilization by increasing film rupture and coalescence tendencies. Elevated temperatures also accelerate foam decay by reducing liquid viscosity and enhancing liquid drainage. In contrast, moderate increases in salinity often improve foam stability by strengthening interfacial films and reducing drainage rates. Dehdari et al. [68] investigated the influence of oil type on foams stabilized with polyvinyl alcohol (PVA) in the presence of surfactants and nanoparticles. Their study demonstrated that heavy oils exerted a more detrimental effect on foam stability than lighter oils. Furthermore, increasing the salinity of the aqueous phase enhanced foam stability in systems containing PVA. Although increasing temperature reduced foam viscosity and accelerated interfacial film drainage, the presence of the polymer significantly improved the thermal stability of the foam system. These findings underscore the important role of polymers in extending the operational window of foam-based EOR technologies under challenging reservoir conditions.

5.2 Alkali–Polymer Flooding

Alkali–polymer (AP) flooding combines the favourable interfacial properties of alkaline solutions with the mobility-control advantages of polymer flooding to achieve enhanced oil recovery. This hybrid technology was developed to overcome the limitations associated with standalone alkaline flooding while simultaneously improving displacement efficiency [47]. Alkaline solutions modify fluid–fluid and rock–fluid interactions by reducing oil–water interfacial tension and altering reservoir wettability. More importantly, alkalis react with naturally occurring acidic compounds in crude oil, particularly naphthenic acids, to generate in situ soaps that facilitate the formation of stable emulsions and ultralow interfacial tension conditions. Despite these advantages, alkaline flooding alone often lacks sufficient mobility control to efficiently propagate the oil bank, particularly in reservoirs containing viscous crude oils. The incorporation of polymers addresses this limitation by increasing the viscosity of the injected fluid and improving the mobility ratio between the displacing and displaced phases. As a result, alkali–polymer flooding simultaneously enhances microscopic displacement efficiency and macroscopic sweep efficiency, leading to improved

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overall recovery performance. The interaction between alkalis and polymers is strongly influenced by polymer chemistry, solution pH, and alkali concentration. The addition of alkali can alter both the ionic strength and alkalinity of the flooding solution, thereby affecting polymer conformation and rheological behavior. In polyacrylamide-based systems, alkaline environments promote hydrolysis reactions that increase the density of negatively charged groups along the polymer backbone. At relatively low alkali concentrations, polymer molecules typically adopt compact coil conformations and exhibit moderate solution viscosities. As alkali concentration increases, the corresponding increase in pH enhances electrostatic repulsion between charged groups, causing polymer chains to expand and increasing their hydrodynamic volume. This expansion results in a significant increase in solution viscosity and improved mobility control. Experimental studies have confirmed these effects. Sheng [69] and Ding et al. [70] reported that the addition of sodium hydroxide to HPAM solutions increased polymer viscosity under saline and elevated-temperature conditions. However, excessive alkali concentrations eventually resulted in viscosity reduction, indicating the existence of an optimal alkali concentration range. Following the reintroduction of waterflooding, the reduction in ionic strength promotes further polymer expansion, increasing flow resistance and diverting injected fluids toward unswept regions of the reservoir. This diversion mechanism contributes to improved sweep efficiency and enhanced oil recovery. Comparable behavior has also been observed in biopolymer systems such as xanthan gum, demonstrating that the beneficial effects of alkali–polymer interactions are not restricted to synthetic polymers alone.

5.3 Surfactant–Polymer Flooding

Surfactant–polymer (SP) flooding is one of the most extensively investigated hybrid chemical EOR technologies because it combines the complementary advantages of surfactants and polymers within a single displacement process. Surfactants primarily improve microscopic displacement efficiency by reducing oil–water interfacial tension, altering reservoir wettability, and stabilizing emulsions capable of mobilizing capillary-trapped oil. While these mechanisms are highly effective for releasing residual oil, surfactant flooding alone often provides limited mobility control and may therefore exhibit poor sweep efficiency in heterogeneous reservoirs and heavy-oil systems. In contrast, polymers primarily influence macroscopic displacement efficiency by increasing the viscosity of the injected aqueous phase and improving the mobility ratio between water and oil. Enhanced mobility control reduces viscous fingering, suppresses channeling, and promotes a more uniform sweep of the reservoir volume. However, polymers generally exert only limited influence on interfacial properties and pore-scale displacement mechanisms. Consequently, the integration of surfactants and polymers into a single flooding formulation enables simultaneous enhancement of both microscopic and macroscopic recovery processes, thereby maximizing overall oil recovery efficiency [71], [76]. The successful implementation of SP flooding requires careful formulation design because incompatibilities between surfactants and polymers can lead to phase separation, precipitation, or reduced flooding efficiency. Furthermore, the sequence of chemical injection plays a critical role in determining process performance. Due to competitive adsorption phenomena within porous media, the chemical injected first can act as a sacrificial agent, reducing adsorption sites available for subsequently injected chemicals while simultaneously contributing to oil recovery. When polymers are injected before surfactants, they can improve conformance control and reduce surfactant adsorption. Conversely, when polymer slugs follow surfactant injection, they help recover bypassed oil by mitigating viscous fingering and improving sweep efficiency during the later stages of the flooding process [71]. Numerous studies have explored the interactions between surfactants and polymers and their influence on flooding behaviour. One of the most important manifestations of these interactions is the modification of interfacial properties as a function of surfactant and polymer

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concentrations. In polymer–surfactant systems, the conventional critical micelle concentration (CMC) is replaced by two characteristic concentration regimes. The first is the critical aggregation concentration (CAC), which occurs at concentrations lower than the CMC and corresponds to the initial association between surfactant molecules and polymer chains. The second is the polymer saturation concentration, which occurs at concentrations exceeding the CMC and is associated with the formation of micellar aggregates in the presence of polymer molecules (Figure 6). These interactions significantly influence solution rheology, interfacial tension, adsorption behavior, and overall flooding performance, making their understanding essential for the design of efficient surfactant–polymer EOR formulations

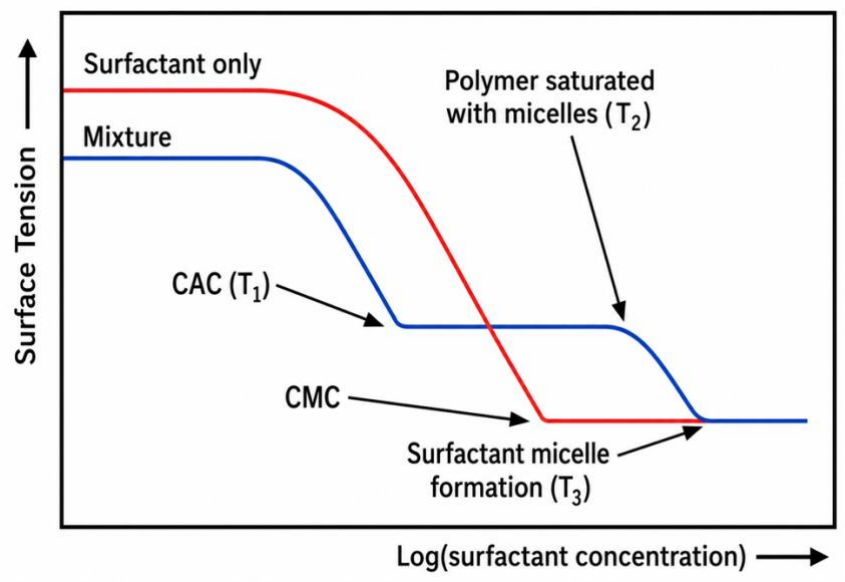

Figure 6. Polymer effect on interfacial tension (IFT) in surfactant–polymer systems [76].

The interactions between surfactants and polymers in surfactant–polymer flooding systems are primarily governed by electrostatic attractions, hydrophobic associations, or a combination of both, depending on the molecular structures and charge characteristics of the individual components. These interactions significantly influence the rheological behaviour, interfacial properties, and overall displacement performance of the flooding formulation. Several studies have demonstrated that surfactant concentration plays a critical role in determining the viscosity and stability of polymer–surfactant mixtures. Afolabi et al. [72] investigated the influence of sodium dodecyl sulfate (SDS) on the rheological behaviour of poly(acrylamide-co-N-dodecylacrylamide) and reported a progressive increase in solution viscosity with increasing surfactant concentration up to the critical micelle concentration (CMC). Beyond this point, a decline in viscosity was observed. The behaviour was attributed to hydrophobic interactions between surfactant molecules and polymer chains, which initially promote intermolecular association but become disrupted once excessive surfactant aggregation occurs. Similar observations were reported by Yusuf et al. [73] for systems containing sodium dodecylbenzene sulfonate and carboxymethyl cellulose (CMC). Their study revealed that viscosity increased until the CMC was reached, after which further increases in surfactant concentration caused viscosity reduction. This decrease was attributed to the formation of hydrophobic microdomains that weakened intermolecular interactions within the surfactant–polymer network. The molecular architecture of surfactants also exerts a substantial influence on polymer rheology. Kalam et al. [74] examined the effects of spacer groups and counterions in polyoxyethylene-based cationic

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Gemini surfactants on cationic polyacrylamide solutions. Increasing surfactant concentration reduced both shear viscosity and elastic properties of the polymer solutions, while elevated temperatures further decreased storage modulus and complex viscosity. However, incorporation of phenyl groups into the surfactant spacer enhanced intermolecular interactions, resulting in improved viscosity and elastic behavior. The authors also observed that chloride counterions provided superior rheological enhancement compared with bromide counterparts. Similarly, Ge et al. [75] investigated the influence of betaine surfactant structure on surfactant–polymer formulations and reported that short-chain betaine surfactants reduced polymer viscosity due to electrostatic shielding effects. In contrast, long-chain betaine surfactants exhibited a positive effect on viscosity at sufficiently high concentrations, highlighting the importance of surfactant molecular structure in determining formulation performance.

To further enhance flooding efficiency while reducing chemical consumption, considerable attention has been directed toward the development of polymeric surfactants. These materials integrate amphiphilic surfactant functionalities directly into polymer chains, producing single-component systems capable of simultaneously modifying interfacial and rheological properties. Although polymeric surfactants generally do not achieve the ultralow interfacial tensions associated with conventional surfactants, they can reduce interfacial tension to approximately 10^{-1} mN m^{-1}, which is sufficient for the formation of stable microemulsions. In addition, these materials exhibit favorable viscoelastic and mobility-control characteristics while maintaining desirable shear-thinning behavior that facilitates injection into reservoir formations. Consequently, polymeric surfactants effectively combine the interfacial activity of surfactants with the rheological advantages of polymers, making them attractive candidates for next-generation EOR formulations [76]. Compared with conventional polymers, polymeric surfactants often display superior solution properties because of the presence of hydrophobic moieties along their molecular backbones. These hydrophobic segments promote intermolecular associations through hydrogen bonding and van der Waals interactions, generating transient network structures that enhance bulk viscosity and viscoelasticity. Kumar et al. [77] investigated an anionic polymeric surfactant derived from Jatropha oil and reported a progressive increase in viscosity with increasing concentration, accompanied by pronounced pseudoplastic behavior at elevated shear rates. Likewise, Babu et al. [78] synthesized a castor oil-derived polymeric surfactant that exhibited non-Newtonian flow behavior and viscosities ranging from 10 to 40 cP, substantially exceeding those of conventional surfactants. Similar findings were reported in studies of polymeric surfactants from natural sources, which showed enhanced rheology and mobility-control potential [79].

5.4 Polymeric Nanofluid Flooding

Although polymer flooding has achieved considerable success in enhanced oil recovery, its effectiveness is often constrained by polymer adsorption, retention, and degradation within reservoir formations. Mechanical, thermal, chemical, and biological degradation processes can significantly reduce polymer performance and limit recovery efficiency. To address these challenges, researchers have explored various strategies aimed at improving polymer stability and functionality under harsh reservoir conditions. Early efforts focused on synthesizing polymers with enhanced temperature and salinity tolerance; however, widespread field implementation was often hindered by high production costs and formulation complexity. More recently, the incorporation of nanoparticles into polymer solutions has emerged as an effective and economically attractive approach for enhancing polymer performance. Interactions between nanoparticles and polymer chains occur through hydrogen bonding, electrostatic attraction, van der Waals forces, steric interactions, and hydrophobic associations, resulting in the formation of polymeric

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nanofluids with unique physicochemical properties. These hybrid materials exhibit improved thermal stability, enhanced salinity tolerance, superior rheological behavior, and reduced adsorption within porous media. Furthermore, polymeric nanofluids can simultaneously modify fluid–fluid and rock–fluid interactions, thereby improving displacement efficiency and overall oil recovery performance [80], [82]. The enhanced rheological properties of polymeric nanofluids under high-temperature and high-salinity conditions have been largely attributed to the formation of strong intermolecular interactions and the protective effect of nanoparticles on polymer chains (Figure 6). Nanoparticles can shield polymer macromolecules from excessive chain contraction and degradation while promoting the formation of stable three-dimensional network structures that preserve viscosity under adverse conditions. As a result, polymeric nanofluids frequently exhibit improved thermal resistance, salt tolerance, and long-term stability compared with conventional polymer solutions. Numerous studies have demonstrated the advantages of nanoparticle-assisted polymer systems. Agi et al. [81] synthesized a starch-based polymeric nanofluid through weak-acid hydrolysis and reported significantly improved rheological properties compared with xanthan gum. Rezaei et al. [82] modified montmorillonite nanoclay surfaces and incorporated them into HPAM solutions, producing polymeric nanofluids with enhanced rheological performance, improved shear resistance, and superior oil recovery.

Several studies have demonstrated the ability of polymeric nanofluids to lower oil–water interfacial tension. Similarly, Sharma et al. [83] observed a significant reduction in interfacial tension following the incorporation of nanoparticles into polyacrylamide solutions. Lower interfacial tension facilitates the mobilization of capillary-trapped oil by reducing capillary forces within pore networks, thereby increasing microscopic displacement efficiency and enhancing hydrocarbon recovery. Wettability alteration is another important mechanism contributing to the effectiveness of polymeric nanofluids. Bera et al. [84] investigated the wettability behavior of guar gum-based polymeric nanofluids and demonstrated a substantial shift in reservoir surface characteristics from oil-wet to more water-wet conditions. The contact angle decreased from approximately 115° to 72° following nanoparticle incorporation, indicating enhanced water affinity of the rock surface. Similar findings were reported by Gbadamosi et al. [85], who observed significant wettability modification in porous media treated with HPAM formulations containing aluminum oxide nanoparticles. Such wettability changes facilitate the release of oil adhered to rock surfaces and improve displacement efficiency during flooding operations.

The stabilization of oil–water emulsions represents an additional advantage of polymeric nanofluids. Stable emulsions can improve oil transport through porous media while preventing phase separation during displacement. Saha et al. [86] reported that formulations containing xanthan gum and silica nanoparticles exhibited excellent emulsion stability and maintained their integrity over extended periods. Likewise, Pal et al. [87] demonstrated that emulsions stabilized by HPAM, silica nanoparticles, and Gemini surfactants possessed superior packing structures and enhanced stability characteristics. Kumar et al. [88] further showed that emulsions stabilized using carboxymethyl cellulose and silica nanoparticles remained stable across a broad temperature range while simultaneously reducing oil–water interfacial tension. These findings highlight the important role of nanoparticles in strengthening interfacial films and improving emulsion durability under reservoir conditions. The combined effects of interfacial tension reduction, wettability modification, emulsion stabilization, and enhanced rheological behavior contribute directly to the superior oil recovery performance of polymeric nanofluids. Numerous displacement studies conducted in sandstone and carbonate reservoir analogues have demonstrated substantial improvements in oil recovery following the injection of polymer–nanoparticle formulations [90].

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Keykhosravi et al. [89]reported that xanthan gum solutions containing anatase titanium dioxide nanoparticles generated an additional recovery of approximately 25% of the original oil in place (OOIP) in carbonate formations. Bera et al. [84] demonstrated an additional recovery of approximately 17% OOIP when nanoparticles were incorporated into guar gum flooding systems compared with conventional polymer flooding. A comprehensive summary of polymeric nanofluid applications and their corresponding oil recovery performances is presented in Table 2.

Table 2. Comparative oil displacement tests using polymer solutions and nanopartical based polymer fluid.

Polymer Type	Solution Conc. (C_p, ppm)	Fluid Viscosity, (μ_o, cP)	Salinity of brine, (ppm)	In.Temp. (T, °C)	Porous Medium Type	Incremental Oil Recovery, (%)
HPAM HAPAM	4 000 ppm	1.6 cP at 60 °C	92000	82	Sandpack	1.67
TVP	2 000 ppm	10 cP	101 000	45	Sandstone	16.4
PAM	2 000 ppm	9.8 cP	101 000	45	Sandstone	12.0
S G ATBS	470 ppm 2 000 ppm	15 cP 41.8 cP	3800	100	Sandstone	10.0
Schizophyllan	2 000 ppm	3.28 cP	167 000	120	Carbonate stone	10.0
ATPs	2500	26	200 000	30	Sandpack	27
HPAM	2500	28	200 000	30	Sandpack	18
SiO_2 - PEOMA	10,000 ppm	-	10 0000	30	Berea sandstone	19,5
Graphene - Gumarabic	50 ppm	-	30 000	90	Berea sandstone	17.12
SiO_2 - $AMC_{12}S$	1100 ppm	-	180 000	110	Sandstone	24.0
SiO_2 - AA/AM	2000 ppm	-	21 800	65	Sandstone	20.1

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6 Limitations of Conventional HPAM and Development of Advanced Polymers

Hydrolyzed polyacrylamide (HPAM) is the most widely utilized synthetic polymer in polymer flooding applications and remains the industry benchmark for chemical enhanced oil recovery (EOR). HPAM is a water-soluble anionic copolymer composed of acrylamide and acrylic acid units, typically produced either through the partial hydrolysis of polyacrylamide (PAM) or by copolymerization of acrylamide with sodium acrylate. Owing to its favorable rheological characteristics, excellent water solubility, resistance to microbial degradation, and relatively low production cost, HPAM has been extensively employed in field-scale EOR operations worldwide [6], [46], [50]. The performance of HPAM is strongly influenced by its degree of hydrolysis (DOH), which typically ranges between 15 and 35% of the acrylamide units. During hydrolysis, a fraction of the amide groups ($–CONH_2$) is converted into carboxylate groups ($–COO^-$), imparting an anionic character to the polymer chain. The resulting charge distribution significantly affects the physicochemical behaviour of the polymer solution, including its viscosity, adsorption tendency, hydrodynamic volume, and solubility in aqueous media. Consequently, the degree of hydrolysis is considered one of the most important parameters governing the efficiency of HPAM in EOR applications. Despite its widespread use, HPAM remains highly sensitive to reservoir conditions. Factors such as temperature, salinity, pH, shear stress, and water hardness can significantly alter its molecular conformation and rheological performance. Elevated temperatures can accelerate polymer degradation, while high concentrations of dissolved salts, particularly divalent cations, may induce chain contraction and viscosity loss. These limitations often restrict the applicability of conventional HPAM in reservoirs characterized by high temperature and high salinity, thereby motivating the development of more robust polymer formulations [24], [25], [51], [62]. To overcome these challenges, considerable attention has been directed toward hydrophobically modified polyacrylamides (HMPAMs), which contain a small fraction of hydrophobic groups incorporated into the polymer backbone. The introduction of these hydrophobic moieties promotes associative interactions among polymer chains, leading to the formation of transient network structures capable of enhancing solution viscosity and improving tolerance to adverse reservoir conditions. These associations may occur either within a single polymer chain (intramolecular association) or between neighbouring chains (intermolecular association), as illustrated in Figure 7 [11], [92]. The relative contribution of intramolecular and intermolecular associations depends strongly on polymer concentration and has a profound effect on solution rheology. At dilute concentrations, intramolecular associations are generally dominant, causing the polymer chains to adopt compact conformations with reduced hydrodynamic radii. As a result, the solution exhibits relatively low viscosity. However, as polymer concentration increases and exceeds the critical association concentration (CAC), intermolecular associations become increasingly significant. The formation of interconnected polymer networks leads to substantial expansion of the effective hydrodynamic volume and a corresponding increase in solution viscosity. The unique associative behaviour of hydrophobically modified polymers provides several advantages over conventional HPAM systems. The transient intermolecular networks formed through hydrophobic interactions contribute to enhanced viscosity retention, improved shear resistance, and greater tolerance to salinity and temperature fluctuations. These properties are particularly valuable in challenging reservoir environments where conventional HPAM often experiences significant performance deterioration. Consequently, hydrophobically modified polyacrylamides have emerged as promising next-generation flooding agents capable of extending the operational limits of polymer flooding and improving recovery efficiency in increasingly demanding oilfield applications [11], [91], [92]. Conventional HPAM and HMPAM exhibit different responses

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under harsh reservoir conditions. Conventional HPAM mainly relies on molecular chain extension to increase solution viscosity; therefore, temperature, salinity, pH, and shear stress can cause chain degradation, contraction, and viscosity loss. By contrast, the hydrophobic groups introduced into HMPAM promote intermolecular associative interactions, forming temporary network structures that improve viscosity retention, salt tolerance, and shear resistance. This associative behaviour explains why HMPAM is often considered more suitable than conventional HPAM for high-temperature and high-salinity reservoir applications [11], [91], [92].

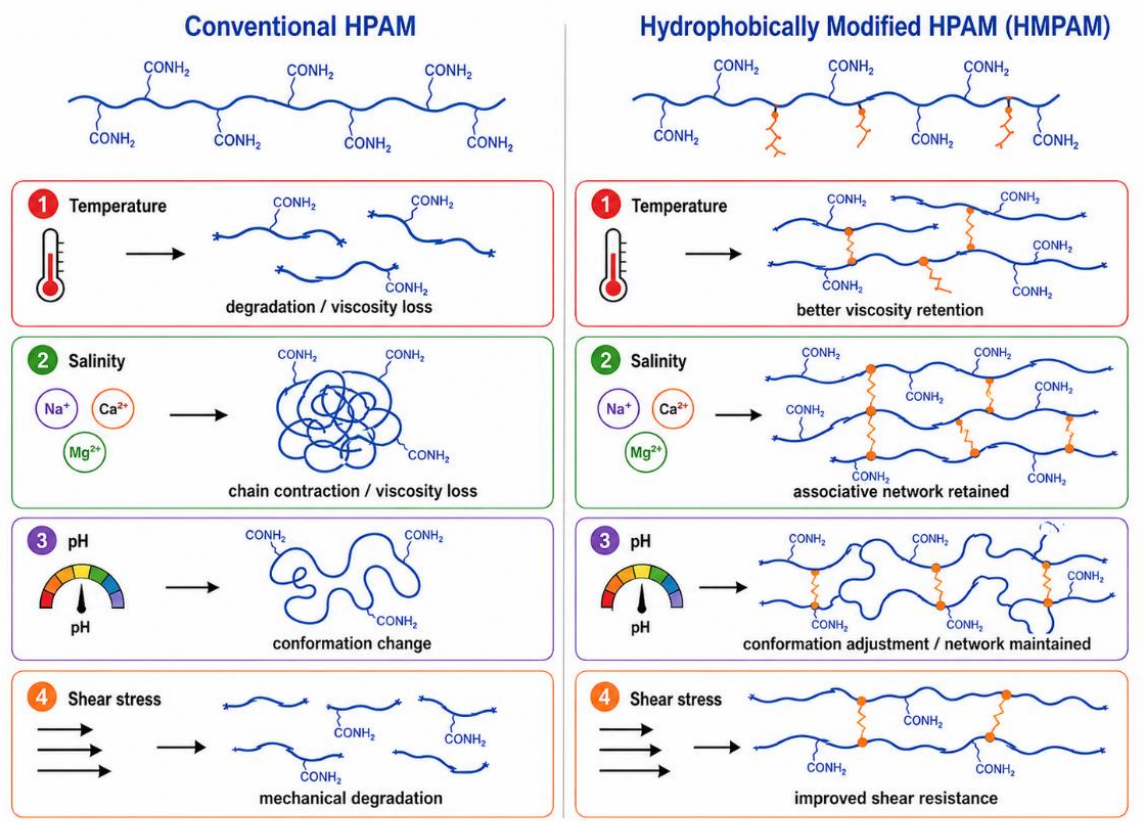

Figure 7. Comparative response of conventional HPAM and hydrophobically modified HPAM (HMPAM) under reservoir-relevant conditions. Schematic created by the authors based on concepts reported in Refs. [91], [92].

7 Polyampholytes for Chemical Enhanced Oil Recovery

7.1 Acrylamide-Based Polyampholytes for Enhanced Oil Recovery

Although HPAM remains the dominant polymer used in chemical enhanced oil recovery, its performance is often compromised under high-temperature and high-salinity reservoir conditions. Consequently, considerable research efforts have been directed toward the development of acrylamide-based polyampholytes, a class of polymers that exhibit exceptional salt tolerance and unique rheological behaviour in electrolyte-rich environments. These materials have emerged as promising alternatives for EOR applications because of their ability to maintain or even enhance viscosity under conditions that typically degrade conventional polyacrylamide-based systems. Acrylamide-based polyampholytes contain both positively and negatively charged functional groups distributed along the polymer backbone. The simultaneous presence of cationic and anionic moieties imparts distinctive solution

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properties that can be tailored through careful monomer selection and polymer architecture design. The balance between cationic and anionic charges can vary with pH, leading to significant changes in polymer conformation and rheological behaviour. Such systems are commonly referred to as annealed polyampholytes and have attracted attention as smart materials capable of exhibiting tunable viscosity and solution properties in response to external stimuli. This pH-responsive behaviour is particularly advantageous for EOR applications, where adaptive rheological properties can facilitate efficient reservoir sweep and mobility control under varying subsurface conditions. The influence of polymer composition on polyampholyte performance has been extensively investigated. McCormick and co-workers synthesized a series of low-charge-density amphoteric copolymers and terpolymers composed of acrylamide, the cationic monomer (3-acrylamidopropyl)trimethylammonium chloride (APTAC), and amino acid-derived monomers such as N-acryloyl valine, N-acryloyl alanine, and N-acryloyl aspartate. Comparative studies involving analogous terpolymers containing sodium 2-acrylamido-2-methylbutane sulfonate (NaAMB) revealed important structure–property relationships. The polymers exhibited excellent solubility in deionized water without phase separation, while the incorporation of NaAMB and N-acryloyl valine increased chain rigidity and enhanced solution viscosity in both freshwater and brine environments. In contrast, polymers containing N-acryloyl alanine and N-acryloyl aspartate displayed greater sensitivity to changes in salinity, highlighting the role of monomer chemistry in governing polymer performance [93], [96].

The ability of polyampholytes to maintain viscosity and swelling behaviour in highly saline environments is one of their most significant advantages for EOR applications. Unlike conventional polyelectrolytes, which generally experience chain contraction in the presence of salts, polyampholytes frequently exhibit the antipolyelectrolyte effect, whereby polymer chains expand as ionic strength increases. This phenomenon enables the retention of favourable rheological properties in reservoirs containing concentrated brines and elevated temperatures, conditions under which traditional HPAM systems often fail. Beyond EOR, acrylamide-based polyampholytes have also found application in drilling fluid technologies. Water-based drilling muds typically contain clay minerals, weighting agents, dispersants, and alkaline additives to achieve the desired rheological and filtration properties.

Table 3. Oil recovery from the sand surface by saline water and amphoteric gel solution [98].

Oil type and oil density, kg.m^{-3}	**Amount of oil adsorbed on sand, mL**	**Gel Concentration, %**	**Amount of desorbed oil, mL**		**Oil Recovery, %**	
			Saline water	Gel solution	Saline water	Gel solution
Light, 814	2.2 (22)	0.5	0.22	1.1	10	50
Middle, 877	3 (30)	4	0.15	1.5	5	50
Heavy, 917	5.2 (52)	4	0.15	1.9	3	36

Amphoteric terpolymers have been successfully employed as viscosity-control additives in such systems because of their remarkable chemical and thermal stability under high ionic-strength

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conditions. Numerous polyampholyte architectures have been developed to enhance salt tolerance and rheological performance. Terpolymers synthesized from acrylamide, sodium styrene sulfonate, and methacrylamidopropyltrimethylammonium chloride have demonstrated excellent resistance to acidic, alkaline, and saline environments. These materials have also exhibited improved drag-reduction properties in aqueous systems. Similarly, terpolymers composed of styrene, metal styrene sulfonate, and 4-vinylpyridine have shown effective drag reduction in a variety of organic media. Graft copolymers based on polysaccharide backbones combined with zwitterionic or paired cationic–anionic monomers have likewise demonstrated excellent thickening and stabilization capabilities in both aqueous and electrolyte-containing solutions. Such characteristics highlight the broad applicability of amphoteric polymer systems and their potential for tailoring fluid properties across diverse industrial processes. Additional innovations include patented technologies aimed at improving oil and gas recovery while simultaneously reducing unwanted water production from subterranean reservoirs. Lightly crosslinked amphoteric gels synthesized from commercially available monomers such as N,N-dimethyl-N,N-diallylammonium chloride, diallylamine, and maleic acid have attracted particular interest because of their exceptional swelling behaviour in concentrated brine solutions. Rheological and viscometric investigations have revealed that the defining characteristic of these amphoteric gels is their ability to absorb water and expand even in highly saline environments. Experimental studies demonstrated that gels dissolved in brines containing salt concentrations as high as 180 g/L retained substantial swelling capacity and favourable rheological properties. Furthermore, model displacement experiments showed that amphoteric gel systems were capable of recovering approximately 75–95% of oil adsorbed on sand surfaces, depending on gel concentration and crude oil characteristics (Table 3) [98]. These results underscore the considerable potential of acrylamide-based polyampholytes as next-generation EOR materials for high-temperature, high-salinity reservoirs where conventional polymer flooding agents exhibit limited effectiveness.

7.2 Salt-Tolerant Polyampholytes for Enhanced Oil Recovery

Salt-tolerant polyampholytes have attracted significant theoretical and experimental interest because of their distinctive charge-regulated behaviour, strong electrolyte responsiveness, and technological relevance to EOR. These polymers belong to an important class of ion-containing macromolecules with broad applications in fluid modification, rheology control, drag reduction, flocculation, and reservoir conformance improvement. Their structures may range from naturally occurring macromolecules, such as proteins and polynucleotides, to synthetic viscosity modifiers designed for demanding industrial environments. Ion-containing polymers are generally categorized as polyelectrolytes or polyzwitterions. Polyelectrolytes contain either anionic or cationic groups along the polymer chain, whereas polyzwitterions contain both positively and negatively charged groups within the same macromolecular structure. Common polyelectrolytes include polyacrylic acid, polymethacrylic acid and their salts, sulfonated polystyrene, and other strong polymeric acids or bases. In contrast, polyampholytes combine oppositely charged functionalities, allowing their conformation, solubility, and rheological properties to respond strongly to changes in ionic strength and solution environment. The rheological behaviour of polyelectrolyte and polyampholyte solutions has been extensively investigated because of their importance as viscosity-control additives in aqueous systems. Acrylamide copolymers containing 2-acrylamido-2-methylpropane sulfonic acid (AMPS) are particularly relevant for oilfield applications owing to their improved stability and tolerance toward salinity. In dilute aqueous solutions, ampholytic terpolymers often exhibit a characteristic globule-to-coil transition as electrolyte concentration increases. This behaviour is especially valuable for EOR because it enables polymer solutions to retain

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or enhance viscosity in saline reservoirs where conventional anionic polymers commonly lose performance.

8 Mechanisms of Polyampholyte-Assisted Oil Recovery

The solution behaviour of polyampholytes is governed by a complex interplay of polymer–solvent and polymer–polymer interactions. Electrostatic interactions among oppositely charged repeating units are especially important and are strongly influenced by charge density, charge balance, charge spacing, monomer distribution, and solution ionic strength. However, electrostatic effects alone cannot fully explain the behaviour of polyampholytes in aqueous media. Other molecular features, including hydrophobic substitution, steric hindrance caused by bulky pendant groups, backbone stiffness, hydrogen bonding interactions, supramolecular interactions, and self-assembly behavior, also contribute significantly to solubility, chain conformation, and viscosity development [94], [95]. Among these properties, salt-responsive behaviour remains one of the most important characteristics driving both academic and industrial interest in polyampholytes for EOR. Acrylamide-based synthetic polyampholytes are particularly promising as electrolyte-tolerant rheology modifiers, drag-reducing agents, and flocculants because they can maintain high solution viscosities under saline conditions while exhibiting stimuli-responsive behaviour. Low-charge-density acrylamide-based polyampholytes containing large fractions of acrylamide units are often preferred because the hydrophilic acrylamide segments promote water solubility at low ionic strength. In many cases, low-charge-density ampholytic terpolymers exhibit superior thickening efficiency compared with highly charged ampholytic copolymers. Polyampholytes containing permanent ionic groups, such as sulfonate and quaternary ammonium moieties, are commonly described as quenched polyampholytes. Their solution behaviour is determined primarily by the ratio of anionic to cationic monomers incorporated into the polymer chain. In contrast, polyampholytes prepared from weak acid or weak base monomers, such as carboxylic acids and tertiary amines, exhibit pH-dependent ionization behaviour. In these systems, the balance between polyampholyte-like and polyelectrolyte-like behaviour is governed not only by monomer composition but also by solution pH. Such materials are referred to as annealed polyampholytes and are capable of undergoing pH-triggered changes in conformation and viscosity. This feature makes them attractive for smart EOR formulations, coatings, and personal care products where controlled viscosity changes are required.

9. Conclusion and Future Perspectives

Polymer flooding remains one of the most technically and economically viable chemical enhanced oil recovery (EOR) technologies for improving sweep efficiency and mobilizing residual hydrocarbons. However, the increasing exploitation of mature reservoirs and the growing prevalence of high-temperature, high-salinity (HTHS) environments have exposed the limitations of conventional flooding agents, particularly partially hydrolysed polyacrylamide (HPAM), which is susceptible to thermal degradation, salinity-induced viscosity loss, and mechanical deterioration. These challenges have stimulated extensive research into advanced polymeric materials and hybrid flooding systems capable of maintaining favourable rheological and interfacial properties under harsh reservoir conditions. This review highlights the significant progress achieved in the development of polymer-based EOR technologies, including polymer–foam, alkali–polymer, surfactant–polymer, and polymeric nanofluid systems. The incorporation of nanoparticles and surfactants into polymer formulations has demonstrated substantial improvements in viscosity retention, thermal stability, salt tolerance, wettability alteration, interfacial tension reduction, and overall oil recovery performance. These hybrid systems provide synergistic mechanisms that address many of the shortcomings associated with conventional polymer flooding and represent important advances toward

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more efficient and adaptable chemical EOR strategies.

Among the various emerging materials, acrylamide-based polyampholytes have attracted particular attention because of their unique salt-responsive behaviour and exceptional tolerance to harsh reservoir environments. Unlike conventional anionic polymers, polyampholytes exhibit the antipolyelectrolyte effect, whereby increasing salinity promotes polymer chain expansion and viscosity enhancement rather than chain contraction. This distinctive characteristic enables the maintenance of favourable mobility-control properties in highly saline reservoirs where traditional polymers typically fail. In addition, polyampholytes demonstrate remarkable thermal stability, resistance to multivalent ions, and broad pH tolerance, making them highly attractive candidates for next-generation EOR applications. Experimental investigations further demonstrate the superior performance of amphoteric terpolymers and amphoteric gels in comparison with conventional HPAM systems. These materials have exhibited enhanced emulsion stability, improved rheological behaviour, and significantly higher oil recovery efficiencies under extreme reservoir conditions. In several model studies, amphoteric gels recovered up to 75–95% of oil from porous media while maintaining functionality in brines containing salt concentrations as high as 180 g L^{-1}. Beyond EOR applications, their excellent viscosity-control capabilities and thermal stability have also enabled their use as rheological modifiers in water-based drilling fluids and other petroleum engineering operations.

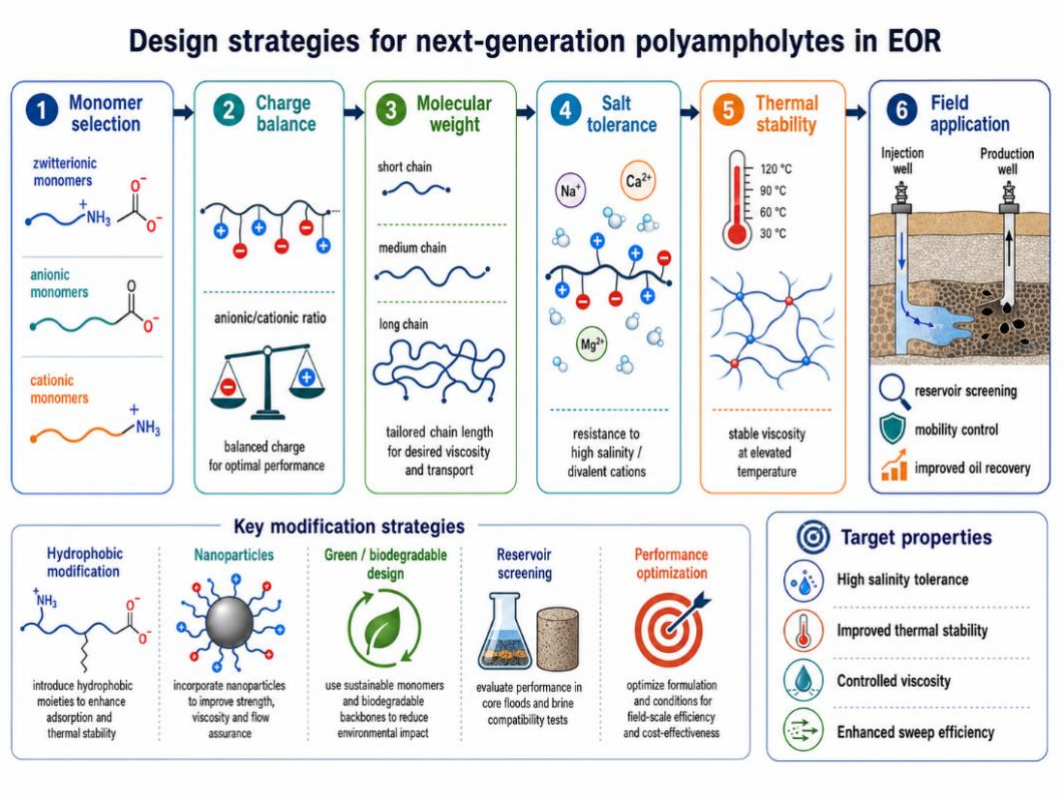

Figure 8. Design Strategies, Functional Modifications, and Target Performance Characteristics of Next-Generation Polyampholytes for EOR.

Despite these promising developments, several challenges remain before polyampholytes and advanced hybrid polymer systems can achieve widespread commercial deployment. Future research

should focus on developing cost-effective and scalable synthesis routes, improving polymer architecture design, and establishing clearer structure–property relationships that govern performance under realistic reservoir conditions (Figure 8). Greater emphasis should also be placed on long-term stability studies, field-scale validation, environmental compatibility, and the evaluation of polymer behaviour in complex reservoir brines containing multivalent ions and mixed contaminants. Looking ahead, the integration of polyampholytes with emerging nanomaterials, smart surfactants, and stimuli-responsive functionalities is expected to define the next generation of chemical EOR technologies. The development of multifunctional hybrid systems capable of simultaneously controlling mobility, modifying wettability, reducing interfacial tension, and adapting to dynamic reservoir conditions offers a promising pathway toward maximizing hydrocarbon recovery from increasingly challenging reservoirs. As global energy demands continue to rise and conventional reserves become progressively more difficult to exploit, salt-tolerant polyampholytes and their hybrid derivatives are poised to play a pivotal role in advancing sustainable and efficient oil recovery technologies.

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The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Supporting Information
Not applicable.

Conflict of Interest
The authors declare no conflict of interest.

AI Use Disclosure
The authors confirm that No AI tools were used to generate scientific results, data, figures, or interpretations. All analyses, conclusions, and scientific content were developed by the authors.

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