Review Article

Smart Polymers Used for Enhanced Oil Recovery Process: A Comparative Study

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Abstract

Application of polymer flooding in oil reservoirs had been widely used for the oil recovery enhancement. However, usage of common polymers like polyacrylamide (PAM) had some limitations, such as high surface absorption, undesirable plugging, polymer concentration limitation, thermal, mechanical and bacterial degradation and also high sensitivity to the reservoir's salinity. In this work, a comprehensive study had been done on five novel types of smart polymers named high molecular weight PAM nanoparticles (NPs), novel core-shell nanostructure of PAM/polystyrene (PS) as protected PAM nanostructure (PPN), cauliflower-like hydrophobically modified PAM nanospheres, novel terpolymers made of three acrylamide (AM), styrene (Sty) and maleic (Ma) monomers, and finally AM-based thermoassociative copolymers (TAP) all of which were designed for smart modification of the mobility ratio to overcome the existed limitations of traditional polymers. Depending on the existed conditions in an oil reservoir, these smart polymers could be a promising candidate for polymer enhanced oil recovery (EOR) method.

Keywords: Smart Polymer; Inverse Emulsion Polymerization; Oil-Water Interface; Enhanced Oil Recovery

Abbreviations

AM: Acrylamide; CEOR: Chemical Enhanced Oil Recovery; EOR: Enhanced Oil Recovery; HPAM: Hydrolyzed Polyacrylamide; Ma: Maleic; NP: Nanoparticle; PAM: Polyacrylamide; PMMS: Acrylamide-Styrene-Maleic Anhydride Terpolymer; PMST: Acrylamide - Styrene Copolymer; PPN: Protected Polyacrylamide Nanostructure; PS: Polystyrene; Sty: Styrene; TAP: Thermoassociative Copolymer; TDS: Total Dissolved Solid; TVP: Thermoviscosifying Polymer.

Introduction

Water channeling from the high permeable path in the porous media makes the efficiency of water flooding low [1]. Considering large amount of oil which remained un-swept in oil reservoirs, leads to the application of EOR methods all of which alter the nature of the reservoir rock and fluid properties to obtain more oil recovery [2]. Polymer flooding is a good example of chemical EOR (CEOR) with a special effect on the reservoir rock and fluid properties [3]. Addition of high molecular weight polymers, such as polyacrylamide (PAM) or hydrolyzed PAM (HPAM) to the aqueous phase overcomes the poor efficiency of the water flooding [4]. Polymer addition increases the viscosity of aqueous phase and modifies the mobility ratio of water to oil [5], and consequently increases amount of oil recovery [6].

However, the performance of common polymers like PAM and HPAM decreases due to their low physical stability and high degradation at harsh reservoir conditions [7-9]. Different solutions have been proposed by researchers to improve the deficiencies of common polymers by modifying their chemical structure. As an instance, replacing some of the AM monomers with more resistant nonionic [10] or anionic ones [11] supresses cation shielding and acrylate moieties precipitating in the polymer chains. Creating a steric hindrance between polymer chains by synthesize of comb-polymers prevents full collapse of the hydrodynamic radius [12]. Synthesize of hydrophobically associating polymers leads to the intermolecular association and viscosity enhancement [13]. Copolymerization of AM monomers with more resistant

monomers such as thermoviscosifying polymers (TVPs) increases the viscosity of the aqueous solution at higher temperature and salinity [14,15] and overcomes the disadvantages of water soluble polymers against harsh environmental conditions. In spite of the benefits of the aforementioned solutions, the structures could be destroyed against extreme biological and mechanical environments such as flowing through pumps, chokes and valves [16]. Besides, regarding the high molecular weight polymers, there is always a limitation of concentration in the classical EOR processes. It should be mentioned that the presence of high molecular weight PAM and its copolymers is necessary to have an optimum efficiency in an EOR process. However, the practical applications need more work due to the complex synthesize procedure, economic problems, and harsh conditions of application. Therefore, the existence of a simple and novel method to provide a new chemical polymer structure for EOR applications is necessary [17].

In this study, a comprehensive review of our previous works regarding the novel methods of producing more effective polymers applicable in harsh reservoir conditions have been gathered. For this purpose, this study is divided into five parts. In the first part, a novel synthesis method of high molecular weight PAM NPs by inverse emulsion polymerization method [18] has been introduced. Then, a novel PAM/PS core-shell nanostructured with a potential of controlling polymer releasement during an EOR process [19] has been discussed in the second part. In the third part, a novel synthesis method of cauliflowerlike amphiphilic copolymers, mainly hydrophobic modified PAM nanospheres by inverse mini-emulsion polymerization and aerosol-photopolymerization method [20] has been analyzed. The synthesis of a new terpolymer including three monomers of AM, Ma anhydride, and Sty by inverse emulsion polymerization to achieve highly hydrophilic–hydrophobic modified PAM [21] has been explained in the fourth part, and finally, synthesis of AM-based TAP with a property of viscosity enhancement versus temperature and salinity has been introduced in the last part.

Novel Smart polymers stable at harsh conditions

High Molecular Weight PAM NPs prepared by inverse emulsion polymerization

Tamsilian., *et al*. in 2016 [18] synthesized high molecular weight PAM NPs by inverse emulsion polymerization of aqueous AM solution in cyclohexane as a continuous phase in the presence of nonionic emulsifier mixtures (Span 20-Span 80). The purpose was to analyze the effect of variation of some reaction conditions on particle size (d) and distribution (PSD), 2nd virial coefficient (A_2), molecular weight (M_w), intrinsic viscosity ([η]), and reaction kinetics (x) to obtain optimal PAM properties for application in EOR. The examined reaction conditions were mixing speed (N), HLB value of the emulsifier system, initiator concentration (C_I), emulsifier concentration (C_E), water in oil (W/O) ratio, polymerization time (t_p), and reaction temperature (T_r).

The results of particle size measurement of PAM NPs are shown in Table 1. Based on this table, a reduction in average particle size and distribution was observed by increasing the mixing speed, increasing emulsifier concentration, decreasing W/O ratio, and decreasing HLB value. Among the examined reaction conditions, all of conditions except for reaction temperature adversely affected the molecular weight and intrinsic viscosity of PAM NPs. Additionally, the monomer conversion of AM was also affected by four factors including reaction temperature, emulsifier concentration, polymerization time, and W/O ratio all of which have contrary effects. Regarding the reaction conditions, PAM particles with average particle diameter less than 73 nm, particle size distribution of 27-285 nm, 2nd virial coefficient of 0.67×10^{-4} mL.mol/g^2, 100% monomer conversion, intrinsic viscosity of 1900 mL/g and finally, viscosity-average molecular weights of 7×10^6 g/mol were obtained as the optimal properties.

Parameter	N	HLB	C_I	C_E	W/O Ratio	t_p	T_r
D	>500 rpm	6.5	-	>1 wt%	< 0.3	-	-
PSD	>500 rpm	6.5	-	>1 wt%	< 0.3	120 min	-
A2	>800 rpm	4.3	-	>1 wt%	= 0.3	120 min	-
M_w	<500 rpm	<6.5	<0.1 wt%	<1 wt%	= 0.3	120 min	60 ^{0}C
[η]	<500 rpm	<6.5	<0.1 wt%	<1 wt%	= 0.3	120 min	60 ^{0}C
X	-	-	-	<1 wt%	= 0.3	>120 min	60 ^{0}C

Table 1: The most appropriate limitations for reaction conditions on characteristics of PAM NPs [18].

PAM/PS core-shell nanostructure for smart EOR process

In another study, Tamsilian., *et al.* [19] synthesized a protected PAM NPs (PPNs) with a hydrophobic PS shell named PAM/PS core-shell nanostructure by one-pot, two-step inverse emulsion polymerization. A schematic structure of the core-shell nanostructure is shown in Figure 1 which can intelligently control mobility ratio in oil reservoirs and overcome weaknesses and limitations of the classical polymer flooding. The synthesize procedure of PAM/PS core-shell nanostructure, protected polyacrylamide nanostructure (PPN), was conducted in two separate recipes: 1- usage of optimum conditions obtained in the first study [18] to inverse emulsion polymerization of PAM NPs and 2- encapsulation of PAM NPs with PS nanolyer. In the first recipe, it was necessary to use an aqueous solution of AM monomer in an oleic phase to produce NPs by inverse emulsion polymerization, and in the second one, the in-situ polymerization of Sty monomers by the usage of a water-soluble initiator was required to encapsulate PAM NPs. According to the experiments, the presence of PS shell protected the active PAM chains from degradation caused by the harsh environment in the reservoirs (i.e. high salinity and high temperature conditions). Under these conditions, PPNs have shown superior properties which makes them strongly applicable for smart nano-chemical EOR.
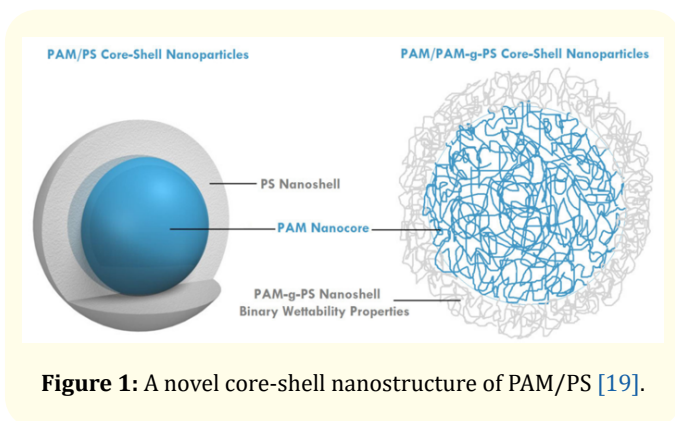

Figure 1: A novel core-shell nanostructure of PAM/PS [19].

The experimental results of released behavior of PPNs in xylene-water interface is shown in Figure 2 and a slow released behavior was observed due to the slow diffusion of high molecular weight PAM throughout PS. This low diffusion rate was because of the prevention of PAM penetration until the PS shell was solved by oil. The low rate of PAM releasement led the particle transferring to the deeper areas of reservoirs, which avoids the desirable water block and oil strands. The blocking of high permeable path in porous media by releasing process (which also increased the viscosity of injected water) decreased water permeability. It is necessary to mention that in order to prevent plugging of the routes in the porous media, the average size of synthesized particles should be

about one order of magnitude lower than the average size of pore and throats. The PS coating in PPN structure was considered as a protective layer for PAM against rapid degradation, mechanical shear stresses, and targeting delivery.
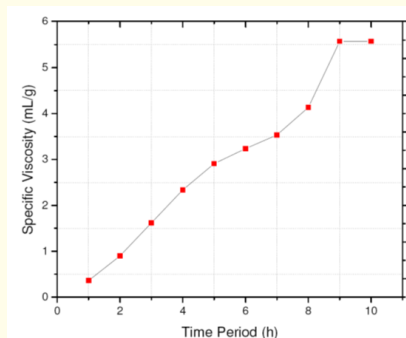

Figure 2: Release behavior of PAM-PS nanostructure in xylene-water interface (C_p=0.2 wt%, T=90 °C) [19].

Comparing PAM NPs and PAM/PS nanostructure

Particle size and distribution

The average particle size and distribution of PAM NPs and PAM-PS nanostructure is shown in Figure 3-a, b. From this figure, the average particle diameter of PAM and PAM-PS NPs are in the range of 50-140 nm and 55-185 nm, respectively; indicating the lower particle size of PAM compared to PAM-PS NPs.
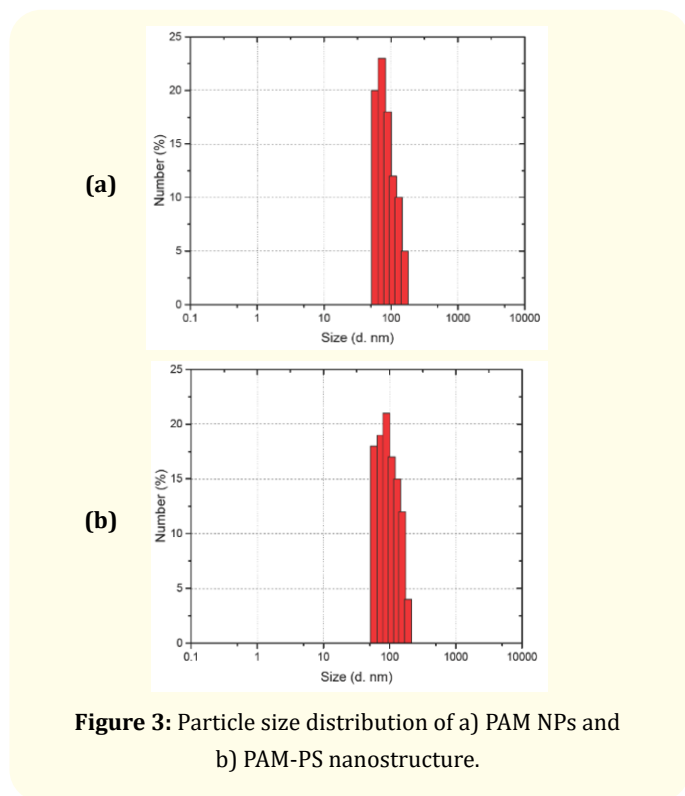

Figure 3: Particle size distribution of a) PAM NPs and b) PAM-PS nanostructure.

IR spectroscopy

The results of IR spectrometry of neat PAM, PS, and PAM-PS nanostructure are shown in Figures 4-a, b, c. The fingerprint region of PS (Figure 4-a) is specified by the peaks before 1700/cm. The PAM particles spectrum (Figure 4-b) shows major peaks at 1673.31/cm and 3212.83/cm, which were attributed to the C=O and NH_2 stretching vibration, respectively. Finally, PAM-PS nanostructures spectrum (Figure 4-c) have peaks at 1183.95 and 1119.55/cm attributed to the NH_2 and C-C bands stretching modes, respectively. In this structure, stretching at 1679.86–1647.65/cm and 597.74/cm were assigned to carbonyl group (C=O) of PAM and C-C band of PS. Besides, the peaks at 2929.28 and 3219.12/cm demonstrated the interaction of CH_2 and NH_2 groups of PAM, respectively. The effect of PS on PAM bands was obviously shown at stretched peaks between 1000 and 1700/cm specially at 1673.31–1454.43/cm. The successfulness of the PAM-PS nanostructures synthesis procedure was proved to be because of the presence of characterization peaks of PS and PAM on PAM-PS nanostructure spectrum. From the first derivative of Differential scanning calorimetry (DSC) curve in Figure 4 (right), the glass transition temperatures (T_g) of PAM, PS, and PAM-PS nanostructures were obtained. The T_g value of neat PS is in the range of 98.9–104.4°C. It should be mentioned that T_g increment was verified at 5-10°C in the case of high molecular weight PAM polymerization. This significant increase was related to the change in the tactility of PS.
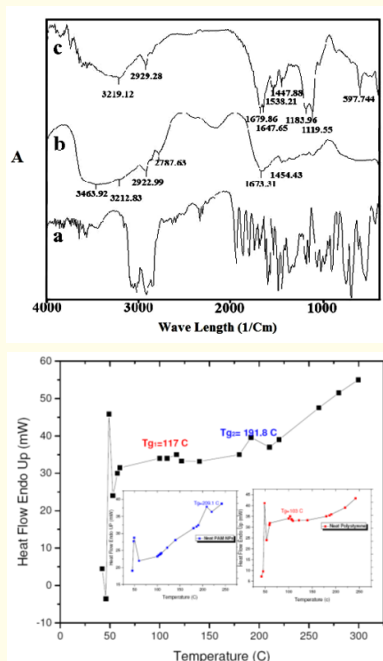
Figure 4: Lleft: IR Spectra and right: DSC test of (a) neat PS, (b) neat PAM, and (c) PAM-PS nanostructure.

Rheological behavior

The comparison between the steady-shear rheological behavior of PAM and PAM-PS aqueous solutions are illustrated in Figure 5. As it can be seen, a Newtonian and shear thinning behavior was observed for both viscosity curves at low and high shear rates, respectively. The shear thinning behavior was attributed to the disruption of the network junction. The difference between PAM and PAM-PS was: 1- the viscosity of the PAM-PS solution was higher than PAM at all examined shear rates. 2- the PAM-PS solution had only two regions of Newtonian and shear-thinning; while the PAM solution had three flow regimes including first Newtonian, the shear-thinning and the second Newtonian regions. Consequently, PAM-PS solution was more favorable in EOR process due to its shear-thinning behavior under high temperature and salinity environment. Hence, it could easily penetrate into the near wellbore with a high shear rate, and go to the deeper area of the reservoir with high viscosity, all of which improve the sweep efficiency in oil reservoirs [22].
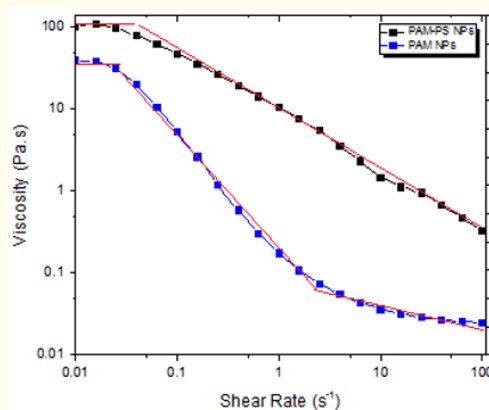
Figure 5: Steady-shear rheology for PAM and PAM-PS nanostructure in pure water (Cp=0.2 wt%, T=90 °C).

Cauliflowerlike amphiphilic copolymers prepared by inverse mini-emulsion polymerization and aerosol-photopolymerization

In another study conducted by Shaban., *et al*. [20], a novel and continuous synthesis of cauliflowerlike amphiphilic copolymers, mainly hydrophobically modified PAM nanospheres was done by inverse mini-emulsion polymerization and aerosol-photopolymerization. The study introduced a novel method of producing spherical PAM, PS and hydrophobically modified PAM (HM-PAM). The results of FT-IR spectra of PAM, PS and poly(AM-co-Sty), known as HM-PAM, prepared by aerosol polymerization is illustrated in Figure 6. The existence of AM and Sty in the HP-PAM structure was confirmed by the presence of both characteristic peaks of PAM and PS in its FT-IR spectra.
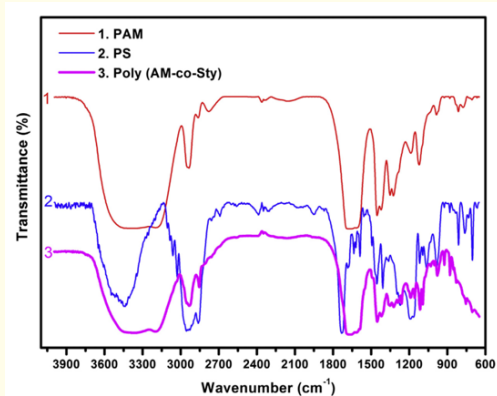
Figure 6: FT-IR Spectra of PAM, PS and poly(AM-co-Sty) generated by aerosol polymerization [20].

According to the study, the novel synthesis method for hydrophobically modified polymers had a great potential to produce novel copolymers with a variety of hydrophobic and hydrophilic monomers. Hence, the study introduced the obtained cauliflower like amphiphilic copolymers as a useful agent for various applications, especially for increasing the viscosity of aqueous solutions and promoting the NPs effect on EOR.

Novel terpolymer prepared by inverse emulsion polymerization

In the final study by Lalehgani., *et al*. [21], new hydrophilic-hydrophobic copolymers and terpolymers with a high efficiency at harsh environmental conditions were produced as an appropriate candidate for EOR purpose in oil reservoirs. The study synthesized several copolymers and terpolymers with different mole percentage of AM, Sty, and Ma monomers via inverse emulsion polymerization method to obtain an optimum one. The study observed a drastic improvement in the efficiency of the oil production compared to common PAM and attributed the observed unique properties to the presence of both hydrophilic (Ma) and hydrophobic (Sty) monomers confirmed by several analyses such as HNMR, elemental analysis, FTIR, SEM, TGA, and DSC. The effect of salinity on viscosity of copolymer (PMST10) and terpolymer (PMMS46) solution at two temperatures of 25 and 80°C is shown in Figure 7. The ascending trend of viscosity by increasing salinity at both low and high temperature which was due to the salting out effect in the solution. The addition of NaCl to the hydrophobically modified polymer solution led to the formation of partial hydrolysis of amide groups and reduction of repulsion between charged groups. The viscosity enhancement of the solution under this situation was done by association of strong hydrophobic groups. Comparing the efficiency of terpolymer and copolymer illustrates a higher solu-

tion viscosity by terpolymer which was due to the presence of Ma anhydride as a linking agent to increase viscosity.
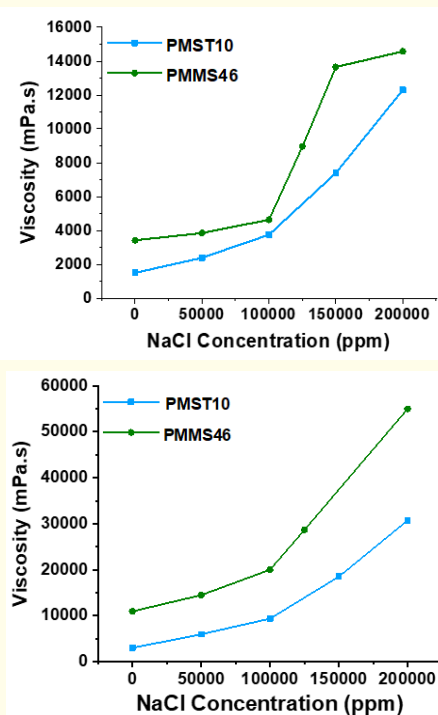

Figure 7: Aqueous polymer solution viscosity versus NaCl concentration for PMST10 copolymer and PMMS46 terpolymer at 0.01 s-1 shear rate at (a) 25 °C and (b) 88 °C, Cp = 2000 ppm [21].

Unlike traditional polymers, the synthesized copolymers and terpolymers aqueous solution exhibited a significant increase in solution viscosity at high temperature, salinity, and shear rate conditions after reaching a critical polymer concentration.

AM-based thermo associative copolymers with a property of viscosity enhancement versus temperature and salinity

The last type of smart polymer prepared by Tamsilian., *et al*. in 2019 was related to the synthesis of AM-based TAP with a property of viscosity enhancement versus temperature and salinity. TAP polymer can be used during the process of NPs synthesis and also during its application as smart nanochemical which was useful in both stability and performance of the NPs. As an example for the smart nanomaterials in this project, schematically the PPNs flooding process is presented in Figure 8. The core-shell PPNs aqueous dispersions were injected into the reservoir through the injection well at time 0 (point 0). The dispersions were pumped to reach the target point 1, the oil phase, for which a time t_1 was necessary, depending on the characteristics of the reservoir. In that point the continuous flow of the PPNs dispersions should be stopped to allow

releasing of Poly(AM-co-St) chains and increased the viscosity of the pushing fluid. The releasing period could be controlled by the characteristic of the protecting shell (the thickness and the solubility characteristic of the hydrophobic co-polymer) and in the present study had shown to be at about 17 h. After that, the displacing high viscosity fluid was necessary to be pushed forward toward the production well (point 2); where due to the change in mobility ratios between the two phases it should enhance the recovery of the oil from the reservoirs. As the Poly(AM-co-St) chains had shown to be more thermally and mechanically stable, one would expect prolonged and improved performance, which was not observed in the performance characterization in laboratory conditions. To simulate the reservoir conditions in the laboratory can be very tricky because of the big difference of the size and pore networks, and might be the main reason why the expected improvement in performance was not demonstrated, despite important improvement of the characteristics of the PPNs.
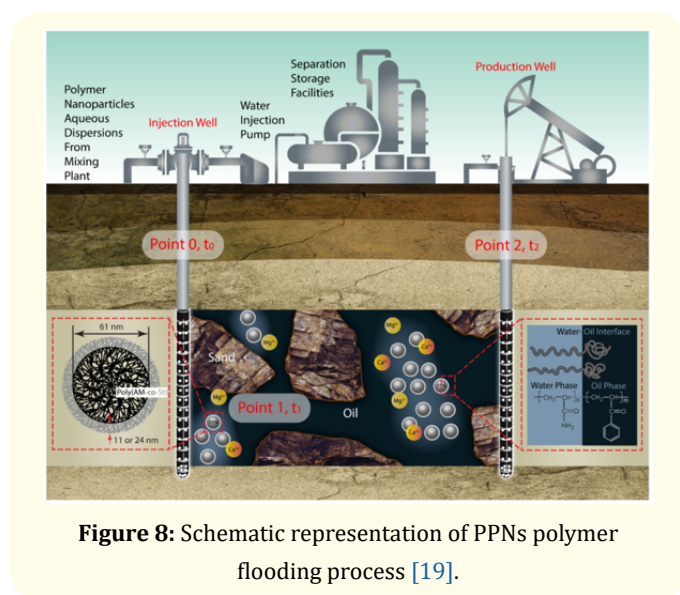
Figure 8: Schematic representation of PPNs polymer flooding process [19].

Conclusion

In this study, five types of smart polymers had been introduced with the aim of overcoming the existed problems of traditional polymers like PAM and HPAM and introducing appropriate polymers for EOR process under harsh oil reservoir conditions. Following results were obtained:

- Optimal properties of high molecular weight PAM NPs for application in EOR were high molecular weight and intrinsic viscosity, polymer particles with nanosized and narrow distribution, and improved colloidal stability of the final dispersions.

- Under high salinity and temperature conditions, PPNs show superior properties which makes them strongly applicable to smart nanochemical EOR. Besides, their adsorption on the rock surface was so low which makes them cost-effective.

- Cauliflower like amphiphilic copolymers were useful for various applications, especially for increasing the viscosity of aqueous solutions which could promote the nanoparticles effect on EOR.

- Terpolymers with hydrophobic-hydrophilic properties and consists of inexpensive and available monomers were good water production control agent in an oil reservoir.

- TAP had a good potential of viscosity increment against temperature in high temperature reservoirs.

Bibliography

1. Hognesen EJ., *et al.* "Waterflooding of preferential oil-wet carbonates: Oil recovery related to reservoir temperature and brine composition". In SPE Europec/EAGE Annual Conference (2005).

2. Føyen T., *et al.* "The Onset of Spontaneous Imbibition: How Irregular Fronts Influence Imbibition Rate and Scaling Groups". In SPE Improved Oil Recovery Conference (2018).

3. Vermolen EC., *et al.* "Low-salinity polymer flooding: improving polymer flooding technical feasibility and economics by using low-salinity make-up brine". In IPTC 2014: International Petroleum Technology Conference (2014).

4. Sheng J. "Enhanced oil recovery field case studies". Gulf Professional Publishing (2013).

5. Alvarado V and Manrique E. "Enhanced oil recovery: field planning and development strategies". Gulf Professional Publishing (2010).

6. Standnes DC and Skjevrak I. "Literature review of implemented polymer field projects". *Journal of Petroleum Science and Engineering* 122 (2014): 761-775.

7. Al Hashmi A., *et al.* "Rheology and mechanical degradation of high-molecular-weight partially hydrolyzed polyacrylamide during flow through capillaries". *Journal of Petroleum Science and Engineering* 105 (2013): 100-106.

8. Dai X., *et al*. "Biodegradation of polyacrylamide by anaerobic digestion under mesophilic condition and its performance in actual dewatered sludge system". *Bioresource technology* 153 (2014): 55-61.

9. Yang MH. "The thermal degradation of polyacrylamide with adsorbed metal ions as stabilizers". *Polymer testing* 19.1 (2000): 85-91.

10. Doe PH., *et al*. "Development and evaluation of EOR polymers suitable for hostile environments part 1: Copolymers of vinyl-pyrrolidone and acrylamide". *SPE Reservoir Engineering* 2.4 (1987): 461-467.

11. Moradi-Araghi A., *et al*. "Development and evaluation of eor polymers suitable for hostile environments: II-Copolymers of acrylamide and sodium AMPS". In SPE International Symposium on Oilfield Chemistry (1987).

12. Wever D., *et al*. "Comb-like thermoresponsive polymeric materials: Synthesis and effect of macromolecular structure on solution properties". *Polymer* 54.21 (2013): 5456-5466.

13. Taylor KC and Nasr-El-Din HA. "Water-soluble hydrophobical-ly associating polymers for improved oil recovery: A literature review". *Journal of Petroleum Science and Engineering* 19.3-4 (1998): 265-280.

14. Chen Q., *et al*. "Thermoviscosifying polymer used for enhanced oil recovery: rheological behaviors and core flooding test". *Polymer bulletin* 70.2 (2013): 391-401.

15. Liu X., *et al*. "Effect of inorganic salts on viscosifying behavior of a thermoassociative water-soluble terpolymer based on 2-acrylamido-methylpropane sulfonic acid". *Journal of applied polymer science* 125.5 (2012): 4041-4048.

16. Maghzi A., *et al*. "The impact of silica nanoparticles on the performance of polymer solution in presence of salts in polymer flooding for heavy oil recovery". *Fuel* 123 (2014): 123-132.

17. Tamsilian Y., *et al*. "Protected Polyacrylamide Nanostructure Used for Enhanced Oil Recovery Process". In 78th EAGE Conference and Exhibition (2016).

18. Tamsilian Y., *et al*. "High molecular weight polyacrylamide nanoparticles prepared by inverse emulsion polymerization: reaction conditions-properties relationships". *Colloid and Polymer Science* 294.3 (2016): 513-525.

19. Tamsilian Y., *et al*. "Nanostructured particles for controlled polymer release in enhanced oil recovery". *Energy Technology* 4.9 (2016): 1035-1046.

20. Shaban M., *et al*. "Facile synthesis of cauliflower-like hydro-phobically modified polyacrylamide nanospheres by aerosol-photopolymerization". *European Polymer Journal* 83 (2016): 323-336.

21. Lalehgani Z., *et al*. "Inverse emulsion polymerization of triple monomers of acrylamide, maleic anhydride, and styrene to achieve highly hydrophilic–hydrophobic modified polyacryl-amide". *Journal of Applied Polymer Science* 136.29 (2019): 47753.

22. Ghannam M and Esmail N. "Flow behavior of enhanced oil recovery alcoflood polymers". *Journal of applied polymer science* 85.14 (2002): 2896-2904.