

Synthesis techniques for polymers applied to enhanced oil recovery

Abstract

A considerable portion of the total oil in place (OIP) present in mature reservoirs cannot be extracted by conventional methods. Therefore, there is an enormous motivation in the development of different techniques to increase the oil recovery. Enhanced Oil Recovery (EOR) is the implementation of several techniques to increase the amount of oil extracted from reservoirs. Its purpose is to mobilize and recover the capillary trapped oil in the reservoirs, and to improve oil sweep efficiency. Dilute aqueous polymer solutions are used, as flooding agents, to improve the mobility index of regular water flooding. Polymers increase water-phase viscosity and reduce the difference between the permeability of the oil and the water phases. Polymers can significantly increase the viscosity of the injected brine by factors up to 20 at very low concentrations. The most used polymer in EOR applications is partially hydrolyzed polyacrylamide (HPAM), a linear copolymer of acrylamide and acrylic acid. Numerous chemical modifications were proposed to HPAM. In this short review, different chemical modifications to the conventional HPAM are summarized and discussed. Furthermore, different synthesis strategies for these water-soluble polymers are analyzed and reviewed.

Keywords: oil, flooding agents, water-phase viscosity, polymer, acrylamide, acrylic acid, water-soluble polymers, aqueous solution, efficiency, aqueous phases

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Abbreviations: OIP, oil in place; EOR, enhanced oil recovery; HPAM, hydrolyzed polyacrylamide; PAM, polyacrylamide; PAA, polyacrylic acid; DMSO, dimethyl sulfoxide

Introduction

The use of water soluble polymers for enhanced oil recovery (EOR) provides an additional chance to extract between 5 to 30% of total oil in place from drilled and mature reservoirs.¹ A big number of patents, mainly from multinational companies, remark the importance of polymers for EOR.² The role of the polymer in the aqueous solution is to increase the viscosity of the displacement solution.³ An important parameter to evaluate the polymer flooding efficiency is the mobility index (M) that depends on the relative permeability and the viscosity of each phase; such parameter between the oil and aqueous phases must be close to the unity to obtain high displacement efficiency.¹

Water-soluble polymers for EOR applications have been successfully implemented in several oilfields.^{4,5} Given the harsh conditions present in oil reservoirs, new problems and limitations arise with the use of water-soluble polymers. They must withstand high salt concentration, the presence of calcium ions, high temperatures (>70°C) and long injection times.^{1,6}

The first polymer used as thickening agent for aqueous solutions was Polyacrylamide (PAM). The thickening capability of PAM resides mainly in its high molecular weight, which reaches values of several millions of grams per mole. PAM is used as the reference model polymer for EOR applications. Partially hydrolyzed polyacrylamide (HPAM) is the most used polymer in EOR. HPAM can be obtained by partial hydrolysis of PAM or by copolymerization of acrylic acid with acrylamide. The optimum acrylic acid content between 20 and 35 wt%.⁷ The presence of electrostatic charges along a polymer backbone is responsible for prominent stretching (due to electric repulsion) of

the polymeric chains in water and, eventually, results in a viscosity increase compared to the uncharged PAM.⁸ When HPAM is dissolved in salted water, a reduction in viscosity is observed.⁹ Yet, alternative ideas to increase the polymer solution viscosity have been studied over the last years. These chemical modifications constitute an important group of polymers for EOR applications named hydrophobically modified polyacrylamide (HMPAM). The association between hydrophobic groups incorporated in the backbone of the polymers affects positively the viscosity of the aqueous phase.³ A small number of hydrophobic groups distributed along the main backbone generates a hydrophobic association between those segments.^{10,11}

Hydrophobic micro-domains are formed when the polymer is dissolved in water, as a result of the association of the hydrophobic groups, above a given hydrophobic monomer concentration. Consequently, an increase of the hydrodynamic volume is observed. This yields a solution with much higher viscosity compared with its non-associative analogue.^{11,12} Many different hydrophobic comonomers,¹³ were used, such as acrylate derivatives, alkyl acrylamides, sulfonates, phenyl methacrylamides, fluorocarbons, vinyl pyrrolidone. The chemical species used as hydrophobic¹⁴ moieties in HMPAM are summarized in Table 1. Although we identified an important number of relevant chemical modifications of HMPAM, we do not claim our final list in the present work to be complete and exhaustive.

Synthesis strategies

Radical polymerization the most used methodology for the synthesis of EOR polymers.² The three main chemical approaches used to synthesize HPAMs are:

- i. The direct free-radical polymerization to produce PAM followed by the acid or base hydrolysis of some of the amide groups along the PAM backbone to produce HPAM

ii. Co-polymerize chosen proportions of acrylamide and acrylic acid. They can be classified as follows:

iii. Polymerize acrylic acid to polyacrylic acid (PAA) followed by the aminolysis of the PAA.

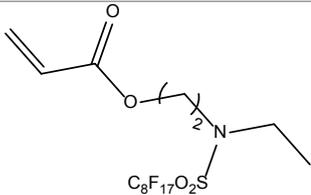
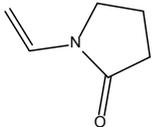
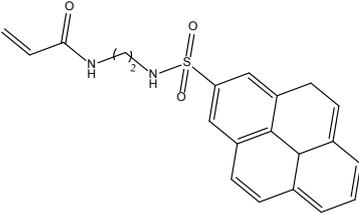
- i. Solution polymerization.
- ii. Dispersed-phase polymerization.
- iii. Precipitation polymerization.

For HPAM or HMPAM, there are different reaction techniques based in the phase scenario of the reactive mixture during the reaction.

Table I Chemical structure of hydrophobic comonomers used in HMPAM for EOR applications

Comonomer	Chemical Structure	Properties Observed in the Copolymer	Reference
Sodium 2-acrylamido-2-methylpropane- sulfonate (NaAMPS)		Salt concentration and high temperature tolerance. Increases water solubility. Hydrophilic spacer in hydrophobic backbone. Increases viscosity	[15-17]
3-(2-acrylamido-2-methylpropane- dimethylammonio)-1- propanesulfonate (AMPDAPS)		Increases water solubility given its zwitterionic behavior. pH sensitive electric charges. Increases viscosity with increasing temperature. Great salt tolerance.	[18,19]
N,N-alkylacrylamides	 N = 7-13 linear carbon backbone, cycles, branched structures	Self-associating hydrophobic moieties.	[20-22]
N,N-dialkylacrylamides	 N=4-14 linear carbon backbone	Improves the self-associating behavior with double hydrophobic tails.	[23,24]
N-isopropylacrylamide		Improves the self-associating behavior with increasing temperature.	[25]
N-phenylmethacrilamides		Improves thermic stability.	[26]
Alkyl acrylates	 N=11-17 linear carbon backbone	Self-associating hydrophobic moieties	[27]

Table Continued...

Comonomer	Chemical Structure	Properties Observed in the Copolymer	Reference
Fluorocarbon hydrophobes		Improves the self-associating behavior compared with the alkyl chains. Increases solution viscosity.	[28]
Vinyl pyrrolidone		Self-associating hydrophobic moieties. Improves chemical stability compared with N-alkyl amides.	[29,30]
N-[(1-pyrenylsulfonamido)ethyl]acrylamide		Strong self-associating hydrophobic moieties. Aromatic structure easily detected by fluorescence.	[31]

The aqueous solution polymerization is the most common and cheapest method used in the production of HPAM where thermal initiators such as peroxide, persulfate, azo-compounds are commonly used. The pH of the aqueous medium determines the final degree of hydrolysis of the product. This process produces a viscous liquid product containing up to 20wt% of the copolymer.

Dispersed-phase or latex polymerization is a more expensive process, carried out in a biphasic liquid mixture; the aqueous reactants are dispersed in an inert organic solvent before the reaction begins. In this case the product is obtained as beads, typically containing 50wt% polymer and 50wt% water. Another option is to use a surfactant for micellar copolymerization that remains nowadays as the most used method for synthesizing HMPAMs.³²

Precipitation polymerization is synthesis technique that could overcome problems associated to solution polymerization and the expensive emulsion process. In this method, the reaction start in a homogeneous mixture of solvent, monomer and initiator (continuous phase). When polymers chains grow above a critical value, they precipitate, forming a separate polymer-rich solid phase. Thus, the reaction medium changes from homogenous to heterogeneous towards the end of reaction.³³ One of the attractive characteristics of this method is that it produces polymers that can be used without any further purification or separation process; with a simple drying step if organic solvents were used as the reaction medium. A slightly different method is the precipitation polymerization in compressed solvents. As the hydrophobic monomers are not soluble in water or polar organic solvents, a compressed solvent can be used to dissolve the hydrophobic and the hydrophilic monomers at the same time. Carbon dioxide is the most promising new solvent for the compressed precipitation reaction.^{34,35} The advantage of this solvent is that high purity copolymers can be obtained without drying or separation process, and that the solvent can be recycled by decompression and recompression.

Our group has experience in different synthesis strategies. Traditional water solution polymerization of acrylamide and/or

acrylic acid in water, solution polymerization in dimethyl sulfoxide (DMSO), emulsion polymerization in cyclohexane and carbon dioxide precipitation polymerization reactions were carried out in our laboratory. Recently, conventional organic-solvent precipitation polymerization in ethyl acetate and in ethyl acetate/cyclohexane mixtures was successfully carried out and the results are being prepared for publications.

Conclusion

This short review highlights the importance of the design of new water-soluble polymers for EOR applications and the different hydrophobic modifications of HPAM to produce self-association in the aqueous polymer solution used for flooding oil wells. Also, a short description of the synthesis strategies for industrial production of these type of materials, is presented. The polymer chemical architecture, and the synthetic techniques used must fulfill the product application requirements. The increase in viscosity is the most important parameter to consider, as a result of the nature of the dilute solution.

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Conflict of interest

The author declares no conflict of interest.

References

1. Sorbie KS, Phill D. *Polymer-improved oil recovery*. Blackie: Springer; 1991. p. 1–11.
2. Wever DAZ, Picchioni F, Broekhuis AA. Polymers for enhanced oil recovery: A paradigm for structure-property relationship in aqueous solution. *Prog Polym Sci*. 2011;36(11):1558–1628.
3. Taylor KC, Nasr-El-Din HA. Water-soluble hydrophobically associating polymers for improved oil recovery: A literature review. *J Pet Sci Eng*. 1998;19(3-4):265–280.

4. Han K, Yang CZ, Zhang ZQ, et al. Recent development of enhanced oil recovery in China. *J Pet Sci Eng.* 1999;22(1-3):181–188.
5. Li G, Zhai L, Xu G, et al. Current tertiary oil recovery in China. *J Dispers Sci Technol.* 2000;21(4):367–408.
6. Lake LW. *Enhanced oil recovery.* Englewood Cliffs, USA: NJ Prentice-Hall Inc; 1989.
7. Morgan SE, McCormick CL. Water soluble polymers in enhanced oil recovery. *Prog Polym Sci.* 1990;15(1):103–145.
8. Stokes R, Evans D. *Fundamentals of interfacial engineering.* New York, USA: Wiley-VCH Verlag; 1997. 736 p.
9. Sukpisan J, Kanatharana J, Sirivat A, et al. The specific viscosity of partially hydrolyzed polyacrylamide solutions: Effects of degree of hydrolysis, molecular weight, solvent quality and temperature. *J Polym Sci Part B Polym Phys.* 1998;36(5):743–753.
10. Argillier JF, Audibert A, Lecourtier J, et al. Solution and adsorption properties of hydrophobically associating water-soluble polyacrylamides. *Colloids Surfaces A Physicochem Eng Asp.* 1996;113(3):247–257.
11. Feng Y, Billon L, Grassl B, et al. Hydrophobically associating polyacrylamides and their partially hydrolyzed derivatives prepared by post-modification. I. *Synthesis and characterization, Polymer.* 2002;43(7):2055–2064.
12. Hill A, Candau F, Selb J. Properties of hydrophobically associating polyacrylamides: influence of the method of synthesis. *Macromolecules.* 1993;26(17):4521–4532.
13. Kathmann EE, White LA, McCormick CL. Water soluble polymers: 70. Effects of methylene versus propylene spacers in the pH and electrolyte responsiveness of zwitterionic copolymers incorporating carboxybetaine monomers. *Polymer.* 1997;38(4):879–886.
14. Hwang FS, Hogen Esch TE. Effects of water-soluble spacers on the hydrophobic association of fluorocarbon-modified poly(acrylamide). *Macromolecules.* 1995;28(9):3328–3335.
15. Branham KD, Davis DD, Middleton JC, et al. Water-soluble polymers: 59. Investigation of the effects of polymer microstructure on the associative behaviour of amphiphilic terpolymers of acrylamide, acrylic acid and N-[(4-decyl)phenyl]acrylamide. *Polymer.* 1994;35(20):4429–4436.
16. Branham KD, Snowden HS, McCormick CL. Water-Soluble Copolymers. 64. Effects of pH and composition on associative properties of amphiphilic acrylamide/acrylic acid terpolymers. *Macromolecules.* 1996;29(1):254–262.
17. McCormick CL, Middleton JC, Cummins DF. Water-soluble copolymers. 37. Synthesis and characterization of responsive hydrophobically modified polyelectrolytes. *Macromolecules.* 1992;25(4):1201–1206.
18. McCormick CL, Salazar L. Water soluble copolymers: 46. Hydrophilic sulphobetaine copolymers of acrylamide and 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate. *Polymer.* 1992;33(21):4617–4624.
19. Kathmann EEL, Davis DD, McCormick CL. Water-Soluble Polymers. 60. Synthesis and solution behavior of terpolymers of acrylic acid, acrylamide, and the zwitterionic monomer 3-[(2-Acrylamido-2-methylpropyl)dimethylammonio]-1-propanesulfonate. *Macromolecules.* 1994;2(12):3156–3161.
20. Shedje AS, Lele AK, Wadgaonkar PP, et al. Hydrophobically modified poly(acrylic acid) using 3-pentadecylcyclohexylamine: synthesis and rheology. *Macromol Chem Phys.* 2005;206(4):464–472.
21. Petit F, Iliopoulos I, Audebert R, et al. Associating polyelectrolytes with perfluoroalkyl side chains: aggregation in aqueous solution, association with surfactants, and comparison with hydrogenated analogues. *Langmuir.* 1997;13(16):4229–4233.
22. Peiffer DG. Hydrophobically associating polymers and their interactions with rod-like micelles. *Polymer.* 1990;31(12):2353–2360.
23. Smith GL, McCormick CL. Water-soluble polymers. 78. Viscosity and NRET fluorescence studies of pH-responsive twin-tailed associative terpolymers based on acrylic acid and methacrylamides. *Macromolecules.* 2001;34(4):918–924.
24. Smith GL, McCormick CL. Water-soluble polymers. 80. Rheological and photophysical studies of pH-responsive terpolymers containing hydrophobic twin-tailed acrylamide monomers. *Macromolecules.* 2001;34(16):5579–5586.
25. Ringsdorf H, Venzmer J, Winnik FM. Fluorescence studies of hydrophobically modified poly(N-isopropylacrylamides). *Macromolecules.* 1991;24(7):1678–1686.
26. Reddy GJ, Naidu SV, Rami Reddy AV. Synthesis and characterization of poly(n-phenyl methacrylamide-co-methyl methacrylate) and reactivity ratios determination. *J Appl Polym Sci.* 2003;90(8):2179–2186.
27. Zhuang D, Da A, Chen J, et al. Hydrophobically modified polyelectrolytes II: synthesis and characterization of poly (acrylic acid-co-alkyl acrylate). *Polym Adv Technol.* 2001;12(11-12):616–625.
28. Chang Y, McCormick CL. Water-soluble copolymers: 57. Amphiphilic cyclocopolymers of diallylalkoxybenzyl-methylammonium chloride and diallyl-dimethylammonium chloride. *Polymer.* 1994;35(16):3503–3512.
29. Sohail K, Khan IU, Shahzad Y, et al. Ph-sensitive polyvinylpyrrolidone-acrylic acid hydrogels: Impact of material parameters on swelling and drug release. *Brazilian J Pharm Sci.* 2014;50(1):173–184.
30. Schulz D, Berluche E, Maurer J, et al. Tetrapolymers of N-vinyl pyrrolidone/acrylamide/salt of acrylic acid/N-alkyl acrylamide. US Patent N°4,663,408; 1985.
31. Senan C, Meadows J, Shone PT, et al. Solution behavior of hydrophobically modified sodium polyacrylate. *Langmuir.* 1994;10(7):2471–2479.
32. Candau F, Selb J. Hydrophobically-modified polyacrylamides prepared by micellar polymerization. *Adv Colloid Interface Sci.* 1999;79(2-3):149–172.
33. Nazaripour, M Rafizadeh S, Bouhendi H. Precipitation copolymerization of acrylamide and acrylic acid: Determination of reactivity ratio by various methods. *E-Polymers.* 2012;12(1):1–16.
34. Romack TJ, Maury EE, DeSimone JM. Precipitation polymerization of acrylic acid in supercritical carbon dioxide. *Macromolecules.* 1995;28(4):912–915.
35. Liu T, Garner P, De Simone JM, et al. Particle formation in precipitation polymerization: Continuous precipitation polymerization of acrylic acid in supercritical carbon dioxide. *Macromolecules.* 2006;39(19):6489–6494.