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Polyacrylamide and its derivatives for oil recovery

Zun Chen

Department: Chemistry

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POLYACRYLAMIDE AND ITS DERIVATIVES FOR OIL RECOVERY

By

Zun Chen

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Approved by

Dr. Thomas P. Schuman, Advisor

Dr. Baojun Bai, Co-advisor

Dr. Yinfa Ma

Dr. Klaus Woelk

Dr. Michael Van De Mark

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This dissertation consists of the following three articles that have been submitted for publication, or will be submitted for publication as follows:

Paper I: Pages 9-111, will be submitted to Polymer Review.

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ABSTRACT

Polyacrylamide is an umbrella term used to describe the homo-polymer of acrylamide and the copolymer of acrylamide with a small amount of other monomers. Owing to their superior property on increasing viscosity and gelling ability in the presence of crosslinkers, polyacrylamides has become the primarily selection for polymer flooding and gel treatment agent in enhanced oil recovery. Recent developments, performance, applications and limitations of polyacrylamides and its derivatives, including copolymers and hydrogels for enhancing oil recovery are reviewed.

A water-free suspension system was developed to synthesize PAMs and PAMs-microgel. Products are dry particle powder and ready to disperse in water. Compared to traditional methods, less surfactant was consumed, and the required energy cost post-treatments, like drying, were not necessary. Hydrophobically modified PAMs and PAM microgels were prepared through this method. Their structures and properties were characterized. The pore modeled oil recovery performance of the microgel was evaluated through a membrane filtration system.

A biocompatible high-strength hydrogel: polyacrylamide/poly (vinyl alcohol) hydrogel with interpenetrating network (IPN) was prepared by in situ free radical solution polymerization/crosslinking of acrylamide and N, N′-methylene-bisacrylamide, as well as chemically crosslinking of PVA with glutaradehyde. Flory–Rehner theory of swelling equilibrium including the ideal Donnan equilibria has been utilized in studying the swelling and mechanical strength of the IPNs. Good linear relationship between the loading of PVA and the effective crosslinking density/strength of the IPN hydrogels had been observed.

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

Symbol	Description
AIBN	azobisisobutyronitrile
AM	acrylamide
AMC_{12}	N-dodecyl acrylamide
AMPS	2-acrylamido-2-methylpropanesulfonicacid
AMQC12	dimethyldodecyl(2-acrylamidoethyl)ammonium bromide
ATBS	sodium acrylamide-tertiary-butyl sulfonate
ATRP	atomic transfer radical polymerization
BPO	benzoyl peroxide
BST	4-butylstyene
$C_{12}AM$	N-dodecylacrylamide
CDG	Colloidal Dispersion Gels
CTAT	cetyltrimethylammoniump-toluene sulfonate
DHAM	N,N-dihexylacrylamide
DMDAC	dimethyldiallyl ammonium chloride
EOR	enhance oil recovery
HAPAM	hydrophobically Associative Polyacrylamide
HMTA	hexamethylenetetramine
HPAM	hydrolyzed polyacrylamide
HQ	hydroquinone
KPS	potassium persulfate
MAA	methacrylic acid

MBAM	methylene-bis-acrylamide
MMT	montmorillonite
$NaAMC_{12}S$	sodium 2-acrylamido-dodecane sulfonate
NaAMPS	sodium 2-acrylamido-2-methylpropane sulphonate
NAM	N-acryloylmorpholine
NAS	N-acryloxysuccinimide
NIPAM	N-isopropylacrylamide
NNDAM	N,N-dimethyl acrylamide
NVP	N-vinyl prrolidone
ODMS	octadecyldimethylmethoxysilane
OOIP	original oil in place
OIP	oil in place
OP	*t*-octylphenoxypolyoxyethylene
PAM	polyacrylamide
PEGDA	polyethylene glycol diacrylate
PEI	polyethyleneimine
PPG	preformed particle gel
Tween 85®	sorbitan trioleate
RRF	relative response factor
SDS	sodium dodecyl sulphate
Span 80®	sorbitan monooleate
TP	5,5,5-triphenyl-1-pentene

TMAEMC	2-trimethylammonium ethyl methacrylate chloride
VN	2-vinylnaphthalene
4-VPPS	4-vinylpyridine propylsulfobetaine

1. PREFACE

Crude oil is an important commodity raw material for the energy and chemical industries. In spite of continued investment and advances in exploiting alternative energy sources, oil and natural gas will continue to be a significant portion of US and global energy portfolios for decades. [1] In the first (primary) stage of oil recovery, the oil is displaced by its own reservoir energy, such as gas drive, water drive, or gravity drainage. In the second stage, external fluids such as water or gas were injected into the reservoir to maintain the necessary pressure and displace the oil towards to the production wells. After the secondary oil recovery, there are still two thirds[2] of the original oil left in the reservoir and in most cases, 40-50% of the original oil in place (OOIP) [3] is not produced (see Figure 1.1.). The tertiary oil recovery, also named the enhanced oil recovery (EOR) uses unconventional chemical methods that target the oil volume remaining in reservoirs after conventional-recovery methods. [4-6]

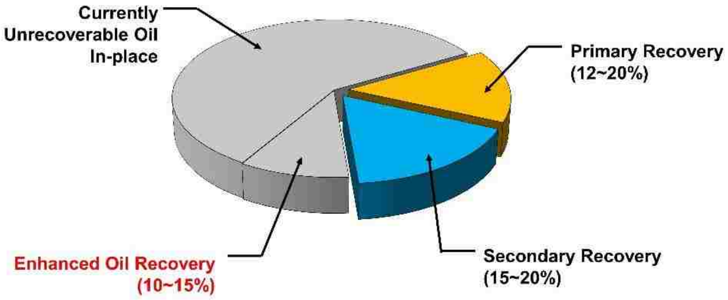


Figure 1.1. Oil production in different stages[4, 5]

It has been proven in field projects that chemical flooding (Figure 1.2.), in especial, polymer flooding is an effective method to improve the oil yield. [7, 8] A typical polymer flood project involves mixing and injecting polymer over an extended period of time until 1/3~1/2 of the reservoir pore volume has been injected. When water is injected into a reservoir, it prefers to follow the path of least resistance to flow (usually the layers with higher permeability) directly to the lower pressure region of the offset producing wells. If the oil in place has a higher viscosity than the injected water, the water will finger through this oil and bypass it. It will result in a lower sweep efficiency and a loss in recovery. [9] The EOR principle of polymer flooding is to increase water viscosity and thus reduce the water/oil, mobility ratio defined as (krw/uw)/(kro/uo) (kro=relative permeability to oil, krw=relative permeability to water, uo=viscosity of oil, uw=viscosity of water) so that the “swept” volume of the petroleum reservoir is increased. Polymer flooding has been applied successfully and has improved oil recovery by 5 to 15% of original oil in place. [1, 9]

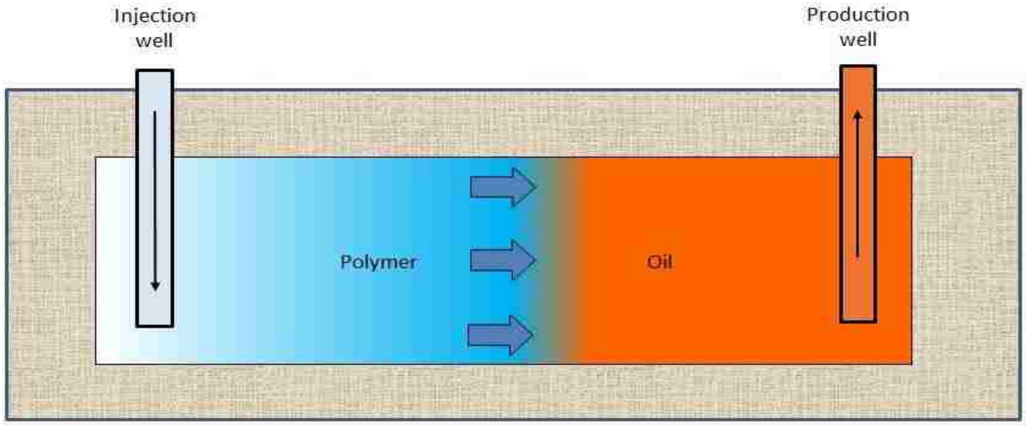


Figure 1.2. Illustration of a typical chemical flooding [10]

Polyacrylamide (PAM)-based polymer is one of the most significant polymer in polymer flooding and has been applied for chemical EOR beginning in the 1960’s. [11-13] A number of PAMs have been developed to increase the viscosity of displacing agent and withstanding harsh environment in reservoirs, [14, 15] including high molecular weight PAM, hydrophobically modified PAM, [16-18] comb-shape PAM, [19, 20] ionic modified PAM[21] and PAMs with combined modification. [22-25]

High molecular weight PAM is one of the earliest polymers employed in polymer flooding. High Mw PAM, through its hydrodynamic volume, increases the viscosity of the fluid so that a large, retained viscosity can be achieved. [16] Meanwhile, temperature and salt resistance can be enhanced to some extent. [26] This kind of PAM has been applied in oilfields more than any other kind of PAMs. [7] However, when subjected to elevated shearing, mechanical degradation could happen, leading to an irreversible loss of viscosity. [27]

Alternatively, such viscosity control can be obtained by taking advantage of hydrohobically associating polymer with lower molecular weight, of which the main polymer backbone is water soluble, whereas it contains a small amount of hydrophobic monomers, such as fatty esters or other saturated carbon units. [18, 28] The main hydrophilic domain renders solubility of the PAMs chain in aqueous phase. For the lipophilic groups distributed along the polymer chain, the amount of them is small, yet, they prefer to associate therefore to form physical linkages due to the unfavorable aqueous solvent conditions. These physical linkages exist both within molecules and between molecules hence rendering a kind of dynamic colloid network structure, which could be broken when susceptible to high shearing, but re-form in a reduced shearing, thus this viscosity loss owing to shearing is reversible.

Based on the development of hydrophobically modified PAMs, both hydrophobic and hydrophilic functional groups were introduced in PAMs polymer chain, resulting in the preparation of comb-shape PAMs. [29, 30] It was reported that comb-shape PAMs has superior salt-resistance through building a hindering structure and generating a random coil configuration. Compared to the traditional polymer chain curling or collapse when subjected to brine, comb-shape PAMs do not fully collapse under a high salinity environment. An extensive investigation for field application has been done in China. [23, 31]

A number of ionic co-monomers were introduced into PAMs and generated another type of PAMs, polyelectrolyte, to increase the salt tolerance of polymer solution. [32, 33] In freshwater, amphoteric polymers are coiled due to the intermolecular attractions by the cationic and anionic groups; however, in brine the polymer will become extended due to charge repulsion so that solution viscosity sensitivity to brine is reduced. Under higher salt concentrations, amphoteric polymers have superior salinity-tolerance and temperature resistance compared to polyelectrolytes with pendant cationic or anionic groups.

Besides the mentioned type PAMs, combined modification methods have been employed in producing PAMs to achieve a desired performance, including preparing PAMs with employing at least two modifications, [34] such as incorporating both hydrophobic and ionic functional element in PAMs, as well as making hybrid PAMs by introducing inorganic functional groups. [35, 36] Figure 1.3. shows the timeline of the development of polyacrylamides for EOR.

Gel treatment is another cost-effective and effective method to enhance oil recovery. Polymer gel treatments of the injection wells are being developed to preferentially limit flow through conduit zones. [37-39] Polymer gels can be cost-effective methods to improve sweep efficiency and reduce excess waste water production during oil recovery. When gels carried by fluid are injected into reservoir, they are prone to preferentially enter channels or fractures with low pressure, and gels may then aggregate or plug a region when the flow path becomes too narrow. Once conduit channels are plugged, flow is shifted to other places of the reservoir, so more of the remaining oil can be displaced. [40]

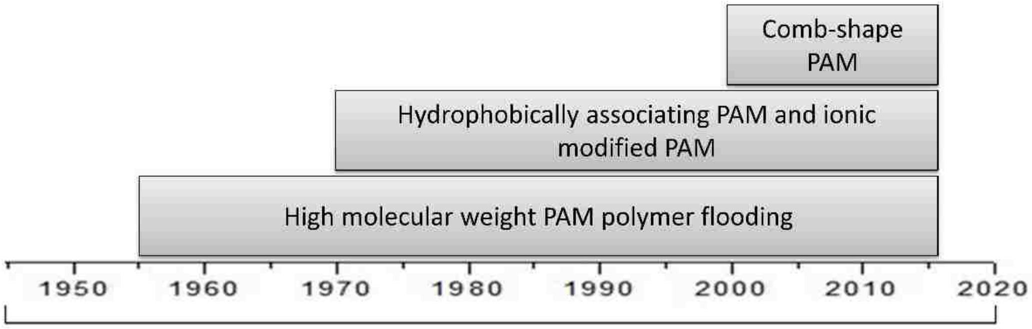


Figure 1.3. Timeline for the Development of Polyacrylamides for Enhanced Oil Recovery

Through proper crosslinking linear PAMs, plenty of three dimensional hydrogels could be prepared with various properties applicable to oil recovery. [41] Currently, two types of gels are commonly applied in controlling conformance of EOR: in-situ crosslinking gels[42] and preformed particle gels (PPGs). [43-45] For in-situ-crosslinking gels, a mixture of monomers and crosslinkers are injected into a target formation to polymerize at the reservoir temperature and form an in-situ gel, that is intended to fully or partially seal a formation region. PPGs are prepared before injection. PPGs are crosslinked dry powder particles forming hydrogels, that can absorb water and expand to several tens or hundreds times their original size when dispersed in water. [46, 47] In-situ gels are generally weak gel whereas PPGs could be strong and also weak gel by adjusting the type and amount of crosslinkers. Hydrogels with different strength could be applied in different area. Weak gels generally have good deformation abilities sealing the porous medium in the deep reservoir.

2. OBJECTIVE OF THIS RESEARCH

Polyacrylamides have intensive applications in oil recovery and other areas. Especially, hydrophobically modified polyacrylamide is one of the most promising type. Currently, the difficulties in preparing modified polyacrylamide arise from the insolubility of the hydrophobic monomers in water. Additionally, traditional polyacrylamides and hydrogel products synthesized in and swollen by water are difficult and energy intensive to isolate from the water phase into dry particles. The mentioned problem can be solved by supposedly developing a water-free polymerization method.

Polyacrylamide (PAM) hydrogel is one of the most common plugging/diverting agents applied in conformance controls and it is preferred become of its low cost, non-toxic and biological inertness, long chain length, capability to preserve their mechanical, morphological and adjustable properties. However, under some strong stimuli of acid or salinity, PAM hydrogels display dramatic shrinkage in size due to ion shielding effect. And, highly swollen PAM hydrogels are generally brittle since they are lacking an efficient energy dissipation mechanism and irregular distribution of crosslinking points. These drawbacks had limited PAMs' applications under some circumstances. Thus, improving the mechanical properties of this kind of hydrogel has become a research target to expand their range of application.

The following studies were planned to pursue these objectives:

1. To develop water-free methods to synthesize PAMs to solve the problem of incompatibility between the acrylamide monomer and hydrophobic co-monomer. To optimize the reaction condition of the system, including the type and amount of surfactants, maximum amount of monomer feeding.

2. To choose or synthesize proper polymerizable surfactant (sufmer) to introduce hydrophobes into polymer chain and make hydrophobically modified PAMs.
3. To study the composition and properties of the products prepared by the water-free polymerization with different characterization methods.
4. To synthesize hydrogels with secondary network to achieve desired properties and study their swelling kinetic, tolerance to salt and pH change.
5. Use proper model and theory to study the hydrogels’ swelling and plugging capabilities.

PAPER

I. Polyacrylamides - Enhanced Oil Recovery

Zun Chen,[1] Thomas P. Schuman[1] and Baojun Bai[2]

[1] Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65401

[2] Department of Petroleum Engineering, Missouri University of Science and Technology, Rolla, MO 65401

ABSTRACT

Polyacrylamide is an umbrella term used to describe the homo-polymer of acrylamide and the copolymer of acrylamide with other monomer (the molar percentage of acrylamide is over 50% generally). Acrylamide monomer has high activity that makes it easier to homo-polymerize and copolymerize with other monomers. Owing to superior viscosity increasing property and gelling ability, polyacrylamides become the primarily selection for polymer flooding and gel treatment agent in enhanced oil recovery. Recent developments, performance, applications and limitations of polyacrylamides and its derivatives, including copolymers and hydrogels for enhancing oil recovery are reviewed. In particular, preparation methodology, polymer architectures, structure-property relationships, lab evaluation and field applications of the polymers are emphasized. High-molecular weight, comb-type, hydrophobically modified associative, amphoteric/zwitterionic, and cross-linked PAM architectures and their utility are described. Structure property relationships are examined. For cross-linked polyacrylamide architectures, the mechanisms of polymer gelling and reversible gelling are detailed.

KEYWORDS

polyacrylamide, oil recovery, polymer flooding, gel treatment

1. Introduction

Crude oil is an important commodity raw material for the energy and chemical industries. In spite of continued investment and advances in exploiting alternative energy sources, oil and natural gas will continue to be a significant portion of US and global energy portfolios for decades.[1] In the first (primary) stage of oil recovery, the oil is displaced by its own reservoir energy, such as gas drive, water drive, or gravity drainage. In the second stage, external fluids such as water or gas were injected into the reservoir to maintain the necessary pressure and displace the oil towards to the production wells. After the secondary oil recovery, there are still two thirds of the original oil left in the reservoir[2] and in most cases, 40-50% of the original oil in place (OOIP) is not produced[3]. The tertiary oil recovery, also named the enhanced oil recovery (EOR) uses unconventional hydrocarbon-recovery methods that target the oil volume remaining in reservoirs after conventional-recovery methods.[4] Among the various EOR methods, thermal methods are primarily used for heavy oils and tar sands; non-thermal methods are normally intended for light oils. For the non-thermal methods, chemical methods have been uneconomic in the past but hold the promise for the future.[2, 4-6] Injecting polymer solution into reservoirs to displace oil, called polymer flooding, can yield a significant increase oil recovery.

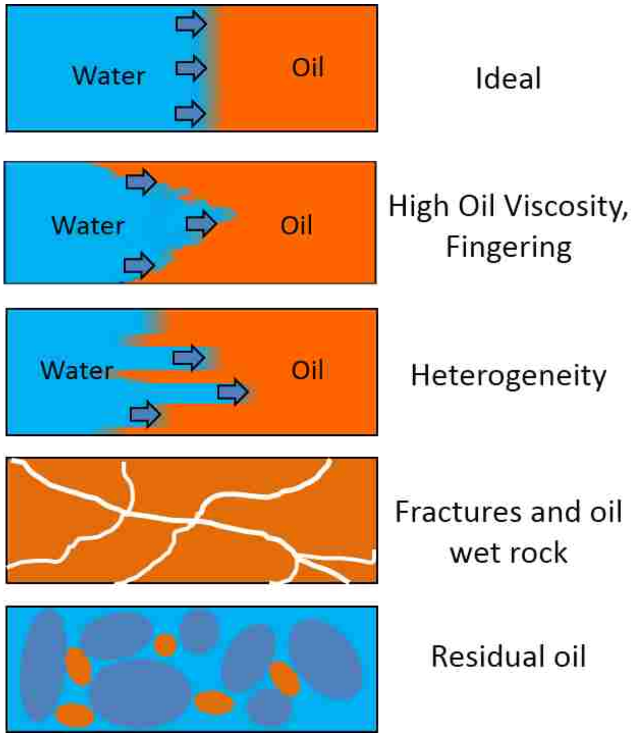


Figure 1. Key issues to be resolved to maximize oil recovery. [7, 8]

In a reservoir, the strata has different layers with heterogeneous permeability. When water is injected into a reservoir, it prefers follow a flow path with lowest resistance. If the injected water has a lower viscosity than the oil in place, the water will finger through the oil and bypass it, resulting a lower sweep efficiency and oil recovery (Figure 1) [7]. The EOR principle of polymer flooding is to increase water viscosity and thus reduce the water/oil, mobility ratio defined as $(k_{rw}/u_w)/(k_{ro}/u_o)$ (k_{ro}=relative permeability to oil, k_{rw}=relative permeability to water, u_o=viscosity of oil, u_w=viscosity of water) so that the "swept" volume of the petroleum reservoir is increased. Polymer flooding has been applied successfully and has improved oil recovery by 5 to 15% of original oil in place.[9-13]

PAM-based polymers were primarily used for chemical EOR beginning in the 1960's.[14-16] In order to get polymer solutions with larger viscosity, PAMs with higher and higher molecular weight were synthesized. Additionally, polymers with ultra-high molecular weight processed better resistance to reservoir environment than lower ones. But these high molecular weight polymer is prone to degrade under shearing comparing to low molecular weight polymer.[17] Partially hydrophobic PAM solved this problem to some extent. It was produced in 70 ~ 80s last century through taking example by the idea from coating industry.[18] Hydrophobically modified water soluble polymers are hydrophobilic macromolecules containing a small fraction of hydrophobic groups which are distributed along the polymer chain or presented as end groups of the side chain.[19] The main hydrophilic domain renders solubility of the polymer chain in aqueous phase. Hycrophobic groups prefer to associate therefore to form physical linkages due to the unfavorable aqueous solvent conditions creating a dynamic transient network. Different from high molecular polymer, which will lose their thickening ability due to easily degradation under high shearing,[20] the self-assembling of hydrophobically modified PAMs is reversible in nature as the hydrophobic interactions can be disrupted when susceptible to high shearing, but re-form in a reduced shearing.[21, 22] Facing harsher environment, a series of salt- and temperature-resistant PAMs were developed. Comb-shaped PAM is a typical one which contains both hydrophobic and hydrophilic side chains and shows excellent salinity resistance when applied to oil field industry since 1999[23, 24]. The introduction of a hindering structure owing to the interaction between hydrophobic and hydrophilic domains generated a random coil configuration that does not fully collapse under a high salinity environment. At the same time, the ionic modified PAMs were designed to make up the defect of hydrophoic groups' water insolubility and also as a "smart" product resisting the harsh salinity environment in real reservoir. The solution viscosity can be modulated by adjusting the identically charged groups in PAMs which can experience repulsion or attraction and cause polymer chain extension or collapse.[17, 25] Recently, in order to get multiple effects, combined modifications were tried through introducing multiple elements to make hybrid PAMs.[26-28]

Among the PAMs for EOR, high molecular weight PAM is a traditional product used in polymer flooding and most field applications about it were conducted; Then the hydrophobic modified polymer, a kinds of PAM with various hydrophobic group were synthesized and got field test since 1970s; [18] From the end of last century, the comb-shaped polymer, such as KYPAM, aroused a lot of attention in China and there was a good effect in real oilfield; As to the promising ionic modified PAM and PAM with multiple modification, the applications of them were limited, however good results were obtained in many lab evaluation. To date, the PF process has been applied successfully in several major Chinese oil fields such as Daqing and Shengli. PF alone contributed approximately 250,000 barrels of oil per day (BOPD) of production in 2004 from these two fields. Incremental oil recoveries of up to 14% of the original oil in place (OOIP) have been obtained in good-quality reservoirs. [29, 30]

To satisfy the need of products for polymer flooding, methodologies to prepare PAMs have experienced a booming developing since the middle last century. A number

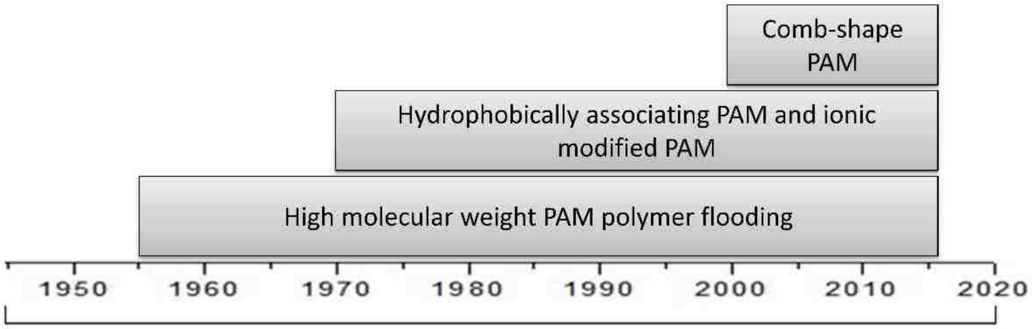


Figure 2. Timeline for the development of Polyacrylamides for Enhanced Oil Recovery.

of methods had been developed to prepare PAM and their derivatives: solution polymerization,[25, 31-35] micellar emulsion polymerization,[36-39] inverse-emulsion and micro-emulsion polymerizations,[40-46] inverse suspension polymerization,[47-49] and living polymerization[50-55].

When injecting water flooding, they may go through channels or fractures with high permeability hence reduce the oil recovery efficiency. With gel treatment, the high permeable zone can be sealed and the pressure in the unswept area will be improved. Therefore the displacing fluid can enter the area with original low permeability hence render the profile control.

On the base of the abovementioned polymers, the introduction of a number of crosslinkers brought surprisingly extended effects and a mass of crosslinking systems were put into field applications[56, 57]. Linear polyacrylamide or modified polyacrylamide which can be cross-linked in present of organic, inorganic and metal ion cross-linkers has become one of the most significant hydrogel system in EOR. Base on different manufacturing methodologies, hydrogels with different chemical properties, physical properties and various particle size can be utilized in a number of areas with different porosity and permeability. For example, bulk gel or larger particle gel can seal larger channel, while small particle can go through low permeability area and plug the tiny holes; gelation system with good chemical stability and can be applied in high temperature reservoir; hydrogel with special functional groups could have unusual properties such as tolerance to salt, base or acid. Thereby to choose a proper synthesis methodology and copolymerized monomer is crucial for the engineers to apply into a characteristic situation and render an effective profile control.

This paper reviews the PAM based polymers and hydrogels utilized in EOR, including the synthesis methodologies, structure and properties of the products as well as their real application in oil field, aiming at drawing more attention of chemists to this surging area of interest so that more advanced products could be developed to meet the tremendous demands for oil industry. In addition, polymers for EOR have been intensively applied in China and a lot of publications are in Chinese, and this paper will also benefit those who are not familiar with Chinese language.

2. PAMs Used in Polymer Flooding

2.1 High Molecular Weight PAMs

High molecular weight PAM is one of the polymers earliest used in EOR.[58-61] High Mw PAM, through its hydrodynamic volume, increased the viscosity of the displacing. Meanwhile, temperature and salt resistance could be enhanced as well compared to water flooding.[62] This kind of PAM had been applied in oilfields more than any other kind of PAMs.

In early 1959, Caudle et al.[16] reported that water driven areal sweep efficiency could be improved by increasing the viscosity of injected solution. In 1964, Pye[63] and Sandiford[64] firstly started experiments to enhance oil recovery by adding polymer to the injected water to form a viscous solution. Then in the following twenty years, much researches had been done in this direction, i.e., to adjust the water-oil mobility ratio and improve the volumetric sweep efficiency through increasing viscosity of injected solution. [64-66]

Based on various initiating systems[58, 67-74] and polymerization methods,[41, 75-79] a series of commercial PAMs of high molecular weight were later developed. For example, Co.Ltd's serial HPAM products possessed molecular masses of 17.5 million Dalton (10^6 Da or MDa) and 14.1 MDa. Pfizer Company developed the Flopaam series of HPAM of 5 to 15 MDa. Dai-Ichi Kogyo Seiaku Co. Ltd. (DKS International, Inc.) had produced the ORP series and Hi-Vis seriesof HPAMs with molecular weights of 24, 27, and 32 MDa. These and other products, from American Cyanamid, Dow Chemical Co. Oil, Gas Chemical Department, and Allied Colloids, had been industrialized and applied infield applications.[80-83] At the same time, numerous synthesis methods had been reported in academic research.

Solution polymerization is one of the most common method to synthesis PAMs. In solution polymerization, all the monomers are dissolved in aqueous solution, and polymerize in the presence of water soluble initiator or redox initiator pair at certain temperature.[84, 85] D'Agosto et al.[32] prepared a long chain copolymer in solution system. This copolymer contained AM, N-acryloylmorpholine (NAM) and N-acryloxysuccinimide(NAS), aiming to produce molecular weights of at least 100 kDa.

Sabhapondit et al. [86] synthesized a high molecular weight (> 1 MDa) copolymer of N,N-dimethylacrylamide-*co*-sodium-2-acrylamido-2-methyl propanesulfonate using N,N-dimethyl acrylamide (NNDAM) and 2-acrylamido-2-methylpropanesulfonicacid (AMPS) by solution polymerization. This high molecular copolymer showed satisfactory results in the core flooding test using 72-150 mesh size unconsolidated sand with a porosity of 42% under different brine concentrations and temperatures (150-300 ℃). Core flooding test showed that about 5.6% OOIP could be recovered by injecting a 2,000 ppm polymer solution. It was known that, the residual oil recovery increased with the increase of temperature. About 11% of OOIP could be recovered as additional oil by injecting a 2000 ppm polymer solution to the unconsolidated sand pack containing one of the Indian crude oils and brine consisting of mono-and bivalent metal ions at 90 ℃. After a water flood, the copolymer was also found to be thermally stable at 120 ℃ aged for at least one month. (Generally, the preferred exposure test time is greater than 6 months.[5])

Inverse emulsion polymerization is another popular methodology, in especial, to prepare high molecular weight PAMs.[87, 88] Aqueous phase containing and oil phase are needed to be mixed to form an emulsion with the assistance of surfactants, and the polymerization of PAMs are conducted in emulsion droplets.

Barari, et al.,[42] through inverse-emulsion polymerization, synthesized a polyacrylamide nanoparticles of high molecular weight. In this preparation, acrylamide monomer was dissolved in water as the dispersed phase and xylene was used as continuous phase. The complex surfactants polyethylene glycol sorbitan trioleate (Tween 85®) and sorbitan monooleate (Span 80®) served as co-emulsifiers. Oil-based initiator benzoyl peroxide (BPO) and water-based initiator potassium persulfate (KPS) were employed to initiate the free radical polymerization. The reaction was performed at 60 ℃ for 150 min and a polyacrylamide with high molecular weight ($\bar{M}_v$~ 8 MDa) was achieved. The PAM particles had average particle sizes generally smaller than 200nm in diameter and particle size distributions in the range of 50 to 400nm.

Wever et al.[89] reported that atomic transfer radical polymerization (ATRP) of acrylamide has been accomplished in aqueous media at room temperature. They used methyl 2-chloropropionate as the initiator and tris [2-(dimethylamino) ethyl]-amine/copper halogenide (CuX) as the catalyst system. A series of linear PAMs possessing apparent molecular weights up to and greater than150 kDa with dispersities as low as 1.39 were produced.

High molecular weight PAMs had been intensively studied in lab evaluation and practical application. A PAM of 15 MD Mw was screened to perform mobility control on two selected pilot layers of Catriel Oeste oilfield, Rio Negro province. It exhibited a permeability contrast of 35:1 and in core tests it yielded average RF values of 34 in one layer and 20 to 7 for another layer. Final oil recovery was 40% for the high permeability core (1400mD), and 58% for the lower permeability core (200mD).[90] Flopaam 3630S (20 MD molecular weight and 25-30% degree of hydrolysis) was tested in field application in Mangala, Barmer Basin, Rajasthan, India.[91] The filed contains medium gravity viscosity crude (10-20 cp) in high permeability sands. The results showed the injectivity test had been very encouraging and demonstrated adequate injectivity of polymer solution of 20-30 cp within the surface injection constrains. After the injectivity test, regular polymer injection has commenced and has been ongoing for several months without any issue. Also it showed there was no significant mechanical degradation of the polymer solution in the wellbore resulting in any significant viscosity loss. During the test no indication of plugging or loss of injectivity was observed.

Zhang et al.[82] tested a polymer with molecular weight of 25 MDa in both lab and field conditions. They pointed out that optimizing polymer solution concentration and molecular weight lead to adsorption and resistance coefficient increased. Under a flow field shear of 10 s^{-1}, elacticity was increased by a factor of 9 and viscosity was doubled when using an enhanced polymer molecular weight from 12 to 25 MDa. Meanwhile the recovery factor was improved from 4.2 to 6.6% when molecular weight increased from 7 to 35 MDa in lab-scale displacing experiments. The field test was conducted in EWN1 block, of area7.75km^2, estimated OIP (oil in place: the total hydrocarbon content of an oil reservoir [92]) of 1606.88*10^4t, and PV (pore volume: total volume of the reservoir * porosity)[93] of 2968.38*10^4 t of the Daqing oilfield, China, Beginning in January 2009, polymer with the MW of 25 MDa and concentration of 2.030 g/L, was injected at 0.22 PV /year. By the end of March 2011, injected polymer solution was 1.0993 g/L. Overall water flow was reduced by 88.5% and recovery was improved 10.8%.

PAM with high molecular weight has an efficient thickening effect[9] with the ability to decrease permeability of the water phase. High Mw PAM is also one of the most effective drag/friction-reducing agents used in hydraulic fracturing. Unfortunately, adsorption of the polymer on the reservoir formation reduces the effectiveness of the recovery of oil and gas from tight, low-permeability formations.[94] Also, polymers of higher molecular weight are easier to mechanically (shear) degrade.[95-97] It was reported this high molecular weight polymer partially hydrolyzed PAM experienced more than 65% loss of their initial viscosity as they flow from the injectors to the producers in some field applications.[98] Additionally, unsuitable polymers with too high a molecular mass may cause oil zone blocking and lead to reservoir damage if the reservoir permeability is low.[99] In contrast, polymers with too low molecular weight can result in poor thickening effects and reduced efficiency. Therefore, choice of appropriate polymer molecular weight is critical to EOR efficiency.

2.2 Hydrophobically Associative Polyacrylamide (HAPAM)

Generally, high molecular weight partially hydrolyzed polyacrylamide (HPAM) could be employed to achieve viscosity control, however, when subjected to elevated shearing, mechanical degradation could happen, leading to loss of viscosity irreversibly.[4] Alternatively, such viscosity control can be obtained by taking advantage of hydrohobically associating polymer with lower molecular weight, of which the main polymer backbone is water soluble, whereas it contains a small amount of hydrophobic monomers, such as fatty esters or other saturated carbon units.[20, 22, 100, 101] The main hydrophilic domain render solubility of the polymer chain in aqueous phase. For the lipophilic groups distributed along the polymer chain, the amount of them is small yet, they prefer to associate therefore to form physical linkages due to the unfavorable aqueous solvent conditions. These physical linkages exist both inter molecules and intra molecules hence rendering a kind of dynamic colloid network structure, which could be broken when susceptible to high shearing, but re-form in a reduced shearing, thus this viscosity loss owing to shearing is reversible. As a result, the preparation of hydrophobically modified polymers has been developed and studied intensively due to their special rheological properties.[102, 103] Much research has been done in this area.[104-107]

Copolymer based on polyacrylamide is one of the most important hydrophobically associative polymers which has been intensively investigated due to its low price, bio-compatibility and widespread applications.[108] Some difficulties in preparing HAPAM arise from the insolubility of the hydrophobic monomers in water. Firstly, mechanical stirring was tried to disperse the hydrophobic monomer into small droplets, but the polymerization did not incorporate the hydrophobic monomers.[21, 109, 110] To overcome this problem, several methods has been developed. The two major of them are: (1) Polymerization in a polar organic solvent or organic solvent/water mixture, in which both hydrophilic and hydrophobic monomers are soluble. Generally, the resulted copolymers are not soluble in such a reaction medium and precipitate out. In conventional solution polymerization, different monomers randomly distribute within the reaction medium and products.[111] However, in a number of developed systems of solvent or solvent/water mixture, chain transfer reaction exerted negative effects on copolymerization and molecular weight.[4] (2). Micellar/inverse emulsion polymerization is the most widely used method for the synthesis of HAPAM, in which hydrophobic monomers are solubilized in a synthetic system by surfactants, generally sodium dodecyl sulphate (SDS).[112-115] It was found the obtained copolymer have an essentially block-like structure, the hydrophobe-rich regions distributed along polyacrylamide backbone. However, sometimes the surfactants served in conventional emulsion polymerization system have some drawbacks, such as poor stability of the latex since the emulsifier attaches on the latex particle only in a physical manner, and some negative effects of the residual surfactants for the properties of the final products.[116-118] Polymerizable surfactants, or surfmers, had been developed to stabilize the emulsion system of synthesizing HAPAM.[118, 119] It was claimed that surfmers could be not only copolymerized into polymer chain, but also strongly attached on to the latex particles with covalent linkage, resulting in better stability of latex than normal surfactant.[118, 120] In summary, the compatibility of hydrophilic and lipophilic comonomers in system is the key point in preparing hydrophobically modified polyacrylamides. In practical terms, to seek out proper solvents is crucial for solution (homogeneous) copolymerization and for micellar (heterogeneous) copolymerization, the importance is to find out effective surfactants.

Rico-Valverde and Jimenez-Regalado[121] synthesized and characterized a series of polymers with telechelic, “multisticker” associative and combined structures using AM, N-isopropylacrylamide (NIPAM) and N,N-dihexylacrylamide (DHAM) via free radical solution polymerization. The viscosity could be maintained up to a certain temperature, called “breaking point”. For telechelic polymers, multisticker, and combined polymers, the breaking points and viscosity were 40 ℃ (~105Pa·s), 50 ℃ (~150 Pa·s), and 60 ℃ (~180Pa·s), respectively. Although the measured viscosities were not very high, the work contributed towards the preparation of polymers whose solution viscosities are not a function of temperature.

Via micellar polymerization, Wang et al.[80] synthesized a new copolymer named KP which has a molecular weight of about 15 million Da but served similar as the high Mw PAM of molecular weight of 30 million Da because a small amount of hydrophobic groups(N-dodecyl acrylamide (AMC_{12}))were introduced into partially hydrolyzed PAM chains. In lab scale evaluation, it showed good stability that maintaining 95% of its initial viscosity after 60 days under salt content 4000mg/L, including 80mg/L Ca^{2+} and Mg^{2+}, 45 ℃. In core-flooding test, it improved oil recovery up to 13% over water flooding.

Identically, through free radical micellar copolymerization, Zhong et al.[122] had prepared water-soluble copolymer, a hydrophobically associating acrylamide modified terpolymer (PAAN) with sodium 2-acrylamido-2-methylpropane sulphonate (NaAMPS) and 2-vinylnaphthalene (VN) as a hydrophobic monomer. Large aromatic groups were incorporated onto the polymer chain forming amicro-block structure so that the rigidity of the molecular chain was increased, resulting in good thermal, salt-thickening, temperature-thickening, and good anti-aging properties for the product. AM, NaAMPS, and sodium dodecyl sulphate (SDS) were first dissolved intoN_2-sparged aqueous media, using NaOH to control the pH value to between 6 and 7 and stirred. VN was then added into the reaction.$K_2S_2O_8$ was employed as the initiator and polymerization proceeded for 16 hours at temperatures maintained under 50 ℃. The copolymer was precipitated into methanol, washed, and dried to isolate the pure VN/NaAMPS/AM terpolymer.

Zhang et al[123] reported a hydrophobically associating terpolymer prepared by AM, 2-trimethylammonium ethyl methacrylate chloride (TMAEMC) and small amounts of 5,5,5-triphenyl-1-pentene (TP < 0.5mol%) through a micellar copolymerization. When copolymer concentration exceeded $0.25gdL^{-1}$, the solution exhibited improved viscosity enhancement properties due to intermolecular hydrophobic association. Additionally, favorable salt tolerance and temperature resistance were demonstrated under applied shear. For preparation, AM was dissolved in distilled water first. The SDS, TP, and TMEMC were added to form mixture solution to which was injected $K_2S_2O_8$ as initiator.

The mixture was stirred for 10 hours under 50 ℃under a nitrogen atmosphere. The polymer was precipitated into methanol, washed, and dried to yield the copolymer solid. The effects of salinity, temperature, and shear rate sensitivities on the viscosity of polymer solution were reported. In salinity within 3% NaCl or $CaCl_2$ brine, the copolymer solution ($0.35 g\cdot dL^{-1}$) provided viscosity over 200 mPa·s while under temperatures up to 75°C the solution maintained a viscosity over 400 Pa·s. Finally, when shear rate was increased from 0 to 80(1/s), the apparent viscosity of the polymer solution decreased from 390 to 220 mPa·s.

Gao, et al.[118] firstly described the combination of a polymerizable surfactant, sodium 2-acrylamido-dodecane sulfonate ($NaAMC_{12}S$), and a strong hydrophobic monomer, N-dodecylacrylamide ($C_{12}AM$) or N,N-didodecylacrylamide ($DiC_{12}AM$), to prepare a water-soluble associating polymer via a new micellar polymerization process. In this process, the surface active monomer with a hydrophobic tail, hydrophilic head group, and polymerizable vinyl double bond acted as both the process emulsifier and as a co-monomer, which participated directly in the copolymerization and thus became a part of the macromolecule. The direct incorporation of emulsifier resulted in improved latex stability and behavior of the final product. For the preparation, the hydrophobic monomer, $C_{12}AM$ or $DiC_{12}AM$ was solubilized in aqueous $NaAMC_{12}S$ first and located in the hydrophobic micellar environment whereas the dissolved hydrophilic monomer AM was located in the aqueous, continuous medium. Through micellar copolymerization under N_2 atmosphere, 45 ℃ for 2 hours initiated by $K_2S_2O_8$, the ternary hydrophobic association polyacrylamide, namely, $C_{12}AM$/ $NaAMC_{12}S$/AM or $DiC_{12}AM$/

$NaAMC_{12}S/AM$ was achieved. This HAPAM with large hydrophobic content and long hydrophobic micro-block possessed strongly associative properties.

Zhou et al.[124] evaluated a hydrophobically associative water-soluble PAM polymer (HAWP) and reported the EOR performance in the J3 well of the SZ36-1 oilfield in Liaodong, Bohai Bay, China. The crude oil was highly viscous, from 13 to 380 mPa·s, whereas the average is 70mPa·s at reservoir condition. After injection of the HAWP for 10 months, water cut [125] (water content) decreased from 95% to 54%, incremental oil reached 25,000 m^3in the corresponding production single well pilot test. In addition, well group pilot tests were done in 2005. The center well covered an area of 0.215 km^2 with the primary geologic reserves of $155.3*10^4$ m^3. After 6 months of continuous injection, water cut began to reduce and oil production increased. The total incremental oil reached 12,000m^3 till Feb. 2007. Deployment of the polymer flooding project has continued since 2008, including eleven wells and thirty-six production wells.[126]

2.3 Comb-type Polyacrylamides

In fresh water, the groups of -COOH or –COONa in traditional PAMs produce exclusion effect causing polymer chain extension so that the polymer solution viscosity increases. While in brine, the interaction between the charges in polymer chain and ions in solution will lead to polymer chain curling or collapse, decreasing the molecular size in solution. Comb-type polymers based on PAM were designed to solve this problem.[23] The introduction of a hindering structure generated a random coil configuration that does not fully collapse under a high salinity environment. The salt resistant comb polymers generally contained both hydrophilic and hydrophobic groups as side chains.[127, 128] Due to the inter-exclusion effects between these two groups, polymer chain were stretched and collapsing phenomenon will be decreased inter and intra polymer chains, hence the polymer chains arrange as comb type in aqueous. Comb polymers are characterized by their high viscoelasticity and good salinity resistance. Consequently, an increased EOR efficiency in brine can be achieved.[129]

Luo, et al.[130] developed a comb-type, salt-tolerant polymer (KYPAM) for EOR (see Figure 3), manufactured by PetroChina, 1999. Several tests were made in comparison to the products MO-4000 from Mitsubishi, Japan and HPAMS DQ2B838 of PetroChina Company, China in a lab scale evaluation. The viscosity of 1000 mg/L (0.1 wt.%) KYPAM solutions in fresh water or brines with 1000 to 19.334 g/L NaCl under different temperatures (45, 70, and 80 ℃) was 30 to 40% higher than the other comparison sample solutions of similar concentration. In the core flooding experiment at 70 ℃, the EOR and the retardation factor (RF) and relative response factor (RRF) values[125] were higher for KYPAM solution than a comparative product HPAM 1285 from British Colloid.[131]

Early KYPAM was described as a copolymer of monomer A and monomer B where A contains one or several unsaturated sites and is a water soluble monomer, while B was characterized by the following structure:[23]

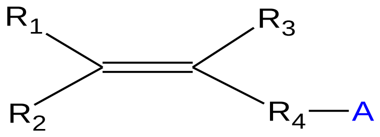


Figure 3. Structure of monomer B in KYPAM. [130]

Where R_1,R_2,R_3 could be H or C_1~C_{12} alkyl, R_4 could be C_1~C_{12} alkyl, C_1~C_{12} alkyl aryl, C_1-C_{12} alkyl ether, or C_1-C_{12} alkyl ester group. A is to contain an ionic functional group insensitive to Ca^{2+} and Mg^{2+}. Monomer B is prepared by dissolving 10-hydroxydecanoate in ethyl alcohol and addition of propylene chloride. The addition of caustic soda solutions drop by drop with heating and refluxing produces the monomer B upon removal of ethyl alcohol and water. A salinity-resistant thickener is then synthesized by adding monomer B, and acrylamide or its derivative, to monomer of Figure 3 with $(NH_4)_2S_2O_8$ and $NaHSO_3$ or AIBN as initiator. The monomer blend is, polymerized over ten hours producing a viscoelastic hydrogel.[130] Since the year 2000, KYPAM has been applied to EOR in reservoirs in China, such as Daqing, Shengli, and Kelamayi. Good performance has been reported there in comparison to conventional PAM. Under the same conditions, KYPAM increased flood solution viscosity by 50% in salt water providing a 100% increase in flooding efficiency. In addition, water cut in oilfield was decreased 15.5% more than using PAM and oil production was enhanced 4.6 times greater than water driving, resulting in a 2% increase in overall recovery ratio.[132]

Based on research into comb-shaped KYPAM polymers, Petrochina Company Limited has developed and now commercially manufactured, braided comb-shaped polymer products. Yuan, et al.[133] synthesized a series of braided comb-shaped, salt-resistant thickening agents using the similar preparation method as KYPAM (summarized above). The copolymerization is a free radical copolymerization initiated by azo-*bis*-isobutyronitrile that results in a polymer suited for assisting liquid flood tertiary oil extraction. The early KYPAM iterative comb-shaped polymer thickening agent is copolymerized with one, or multiple, water soluble unsaturated compound(s), such as acrylamide, vinyl pyrrolidone, 2-acrylamide-2 methyl propane sulfonic acid, acrylic acid and mixtures thereof, and a series monomer analogous to Figure 3 (depicted in Figure 4).

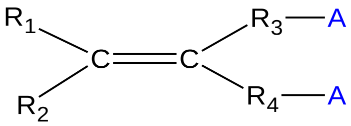


Figure 4. Structure of monomer in KYPAM. [130]

In Figure 4, R_1 and R_2 represent either a H or C_1-C_{12} alkyl, R_3 and R_4 are C_1-C_{12} alkyl, C_1-C_{12} alkylaryl, C_1-C_{12} alkyl ether, or a C_1-C_{12} alkyl-ester group. The structure variable “A” is carboxyl (COOH), alcohol (OH), or sulfoxyl (SO_3H). The iterative polymer was tested in Daqing oilfield where the results showed the viscosity of the KYPAM comb-shaped, salt-resistant industrial polymer maintained solution viscosity above 40 mPa·s, ~41.2% higher than that of conventional polyacrylamides.

Recently, Xu, et al.[134] reported a nonionic but amphiphilic, comb-type polyacrylamide structure. They first synthesized a nonioinic, amphiphilic macro-mer, *t*-octylphenoxypolyoxyethylene(OP) acrylic ester (OPAE) by esterification of acrylic acid (AA) with OP. The macro-mer was then copolymerized with acrylamide (AM) under a free radical initiation system and alkaline environment. Upon precipitation in acetone, a comb-type polymer of mixed structure, P(AM-OPAE) and P(AM-AANa-OPAE) with 17 mol.-% degree of hydrolysis was obtained. Solutions of the P(AM-AANa-OPAE) have a significantly higher apparent viscosity than HPAM solutions under identical concentration and shear rate conditions. Since both hydrophilic and hydrophobic side chains were introduced into the backbone of the polymers, the apparent inter-chain repulsion reduces polymer coil collapse in solution, the curling behavior, so that the salt-resistance and shearing-resistance were also improved compared to HPAM solutions. In field applications, KYPAM was tested at the Lamadian oilfield, Daqing, China, which was of area 3.45 km^2. From May, 2001 to December, 2002, KYPAM improved average oil production rate by a factor of 4.6, which correspondingly increased oil recovery by 2%, compared to ultra-high molecular weight PAM solutions. Since 2003, KYPAM has been widely used in the Daqing oilfield. Similar practical application was implemented in the Shengli oil field, from 2001 to 2003(see Table 1. KYPAM solutions were also applied in the Huabei Oilfield, which increased the oil production rate from 37 to 71 tons per day, totally 12,000t and water-cut was decreased from 92.1% to 89.2%.[135-137]

Table 1
KYPAM Polymer Performance in Shengli Oilfield.[138]

Polymer	Water Type	Wells	Polymer Consump-tion	Water Content Decrease	Incremental Oil Per Day
MO-4000 (Janpan)	Fresh	Water well: 22 Oil well:45	2775.4 t	2.6%	1.62t
KYPAM	Fresh	Water well: 16 Oil well:28	1530.0 t	3.8%	2.65t
KYPAM	Waste	Water well: 10 Oil well:16	959.2 t	2.2%	2.7t

2.4 Ionic Modified Polyacrylamides

PAM based polyelectrolytes is one of another type of important polymers utilized EOR. PAM based polyelectrolytes is one of another type of important polymers utilized EOR. They are classified three types: anionic, cationic and amphoteric polyelectrolytes, due to different ionic groups bearing along the PAMs’ backbone or sidechain.[17] These polymers are widely employed in EOR as viscosity control agents for enhanced oil recovery, drilling fluid additives, and also for modifying flow and stability properties of aqueous solutions and gels.[139, 140] They also can be mixed in surfactant solution working as interface stabilize taking advantage of electrostatic forces in other flooding.[141] In preparing hydrophobically modified PAM, the main method is to introduce hydrophobic associative groups onto the PAM chain. Compared to hydrophobe, ionic co-monomers are water soluble and regarded as “environmental-friendly” and “designable” material solutions, which has drawn recent attention.[33, 142-146] These polyelectrolytes are synthesized by free radical polymerization of acrylamide and their derivatives by the copolymerization method, which includes solution, precipitation, and emulsion techniques.[17, 147, 148]

Fernandez[143] presented cationic, water-soluble polymers prepared by copolymerizing AM, N-vinyl prrolidone (NVP), and methacrylamide propyl trimethylammonium chloride (MP) via free radical polymerization in aqueous solution. Characterization indicated AM and NVP tended to form alternating copolymers during the polymerization. The introduction of NVP effectively limited the hydrolysis of the primary amide groups in the polymer chain and allowed formation of inter-chain hydrogen bonding so that thermal stability was improved.

Zou, et al.[144, 149] synthesized a series of water-soluble anionic acrylamide polymers with cyclodextrin side chains, which endow a polymer molecular recognition function. The cup-type structure appears to hold surfactant resulting in a 20% reduction of the surfactant loss caused by stratum absorption in the process of polymer/surfactant flooding. First, the allyl-β-cyclodextrin (allyl-β-CD) was synthesized from β-CD and allyl bromide using sodium hydroxide as an alkaline catalyst. A series of copolymers were then prepared from allyl bromide, sodium acrylate, and acrylamide at various mole ratios under redox initiated free radical polymerization in the presence of achelating agent.

Through the introduction of both cationic and anionic groups, amphoteric polymers are synthesized. In freshwater, amphoteric polymers are coiled due to the intermolecular attractions by the cationic and anionic groups; however, in brine the polymer will become extended due to charge dilution of the ionic groups in the molecular chain by the salt ions in the brine so that solution viscosity sensitivity to brine is reduced. Under higher salt concentrations, amphoteric polymers of larger molecular weight have superior salinity-tolerance and temperature resistance compared to polyelectrolytes with only pendant cationic or anionic groups. When the numbers of cationic and anionic groups are equal, i.e., the average net charge of the macromolecular chain equals zero, the polymer chain extension remains approximately constant so that the solution viscosity changes only slightly in reservoirs with different mineral salt concentration. Good salinity resistance could therefore be achieved.

Rodríguez, et al.[145] synthesized groups of anionic and zwitterionic modified PAMs using a gel polymerization process and studied the rheology of the products as well as mixtures. One modified PAM was a copolymer (PAM-S) of AM with the sodium salt of 2-acrylamide-2-methyl-1-propane sulfonic acid and the other consisted of the zwitterionic copolymer (PAM-Z) of AM with a sulfobetaine methacrylate monomer. The obtained bulk gel was cut into small pieces, dried, and fine powders were achieved. Solutions were prepared by mixing the polymer powders, brine and the surfactant cetyltrimethylammoniump-toluene sulfonate (CTAT). The mixed polymer and surfactant formed worm like, elongated micelles and a viscosification synergy behavior was explored. In the wormlike micellar system, the surfactant associations worked similar to polyelectrolyte associations to form shear-reduced cooperative structure sand shear-thickening behavior together with the two modified PAMs so that overall a shear thickening behavior was observed.[150] Furthermore, greater increases in micellar length promoted the solution viscosity due to formation of an entangled micellar network. Gui, et al.[151] synthesized a zwitterionic PAM/VPPS copolymer containing sulfobetaine groups by copolymerizing AM and 4-vinylpyridine propylsulfobetaine (4-VPPS). They first prepared 4-VPPS monomer through the ring opening reaction of 1,3-styrene with 4-vinylpyridine (4-VP).[152] The 4-VPPS product was then copolymerized with AM, utilizing redox initiation in a NaCl solution. After precipitation in acetone, washing by water, and drying, a fine powder was obtained.

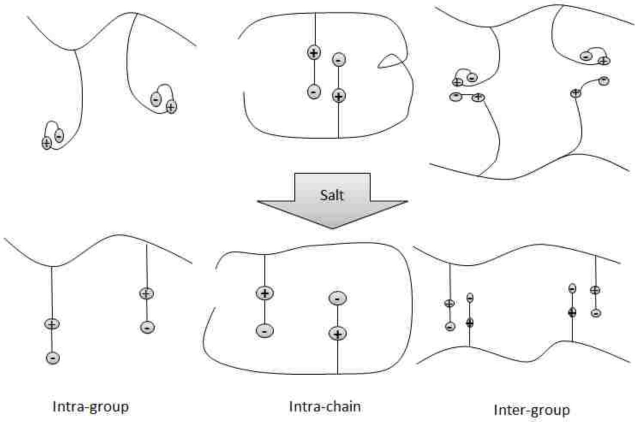


Figure 5. Schematic of AMVPPS copolymer conformations in aqueous NaCl solution. [151]

The copolymer in solution showed good viscosity building performance due to electrostatic associative interactions despite the presence of salt. For thermo-stability, TGA and DTA tests demonstrated that as the VPPS content was increased from 0-to 10mol.-% in the copolymer, the decomposition temperature of the copolymer was improved from 263to 388 ℃). With regard to thickening ability, the zwitterionic copolymer tended to form cyclic or head-to-tail structures, as shown in Figure 5

Gaillard, et al.[146] evaluated anionic co- and terpolymers of AM monomer in lab scale EOR performance. Results showed that polymer flooding could be successful in reservoirs with relative high temperature and poor water quality (in presence of oxygen, iron, and radical; under 90-120 ℃). Theco- or terpolymers were synthesized from AM, sodium acrylamide-tertiary-butyl sulfonate (ATBS), and NVP monomers. The viscosity of polymer solutions aged up to 120 ℃ could typically retain 60 to110% of their initial viscosity after a few months compared to a 10 to 40% viscosity retention of conventional PAM systems. At 100 ℃, the viscosity of the polymer solution was stable for over 60 days in the presence of 200 ppb of oxygen. At 120 ℃, radical degradation resulted, to cause a viscosity drop of the solution.

Aparecida de Melo, et al.[153] presented the application of polyelectrolytes with negative charge in the oilfields of Carmopolis, Buracica, and Canto do Amaro, Brazil. Niu, et al.[154] published the field application results for an amphoteric PAM copolymer in China.

2.5 Combined Modified Polyacrylamides and Hybrid Polyacrylamides

Hydrophobically associating polyampholyte successfully introduces the combined effects of electrostatic attraction between opposite charges and hydrophobically associating interactions between intra-and/or intermolecular chains in a single co-polyacrylamide. Concurrently, the two different effects can exert influence towards each other, which contributes special polymer solution properties.[155]

An, et al.[156] synthesized one form of HAPA under free radical micellar polymerization using the monomers AM, AA, and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (AMQC12). They first prepared the ionic surfmer, i.e., surfactant monomer AMQC12, from N,N-dimethylethylenediamine, methylene chloride and dodecyl-1-bromide. Copolymerization of the surfmer alkene with AM and AA generated the targeted polymer material. The solution viscosity of the HAPA polymer increased with addition of NaCl due to an anti-associative, polyelectrolyte effect.

Zhong, et al.[27] polymerized terpolymers (PADB) with AM as the main monomer, 4-butylstyene (BST) and dimethyldiallyl ammonium chloride (DMDAC) as the hydrophobic monomers, by the micellar free radical copolymerization technique. When the polymer concentration was increased above the critical association concentration (CMC), the viscosity of PADB was dramatically improved. The polymer provided an effective viscosification effect in 2.222 $\mathrm{mol\cdot L^{-1}}$ NaCl solution, exhibiting good salt resistance. Large hydrophobic aggregates were formed in aqueous 0.1g $\mathrm{dL^{-1}}$ PADB where the hydrophobic structure became further enlarged when enhancing the concentration. These microstructures were disrupted by adding small amounts of salt, resulting in decreased solution viscosities. However, with further increases of NaCl concentration, aggregates were again increased and formed dendritic, associating structures, leading to enhanced solution viscosity.

Organic-inorganic hybrid composites are an emerging class of materials holding significant promise because usually they have the combined/synergistic properties.[157, 158] While in polyacrylamides, the functional groups, such as -NH_2, -COOH, can form Van der Waals force, hydrogen bonding, electrostatic interaction and ionic force with inorganic particles and clay.[159, 160] For clay incorporation, few polymer chains can penetrate the clay's interlayer space and then entangle to each other therefore to form a kind of reinforcement (weak)[161], see Figure 6. While obvious viscosity increment is brought by a kind of extra gallery viscous force (similar to friction force)[162] (dominate reason for viscosity increasing). For nanoparticle incorporation, similar force occur due to large surface area (see Figure 7). There have been a lot of attempts to import the inorganic materials to polyacrylamides system[163, 164].

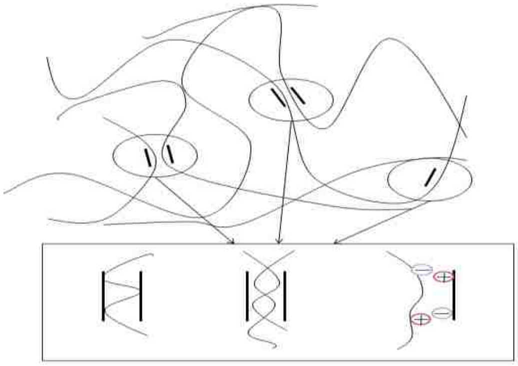


Figure 6. Structure model of the gelation of polyacrylamide/nanoclay gelant solution. **[**161]

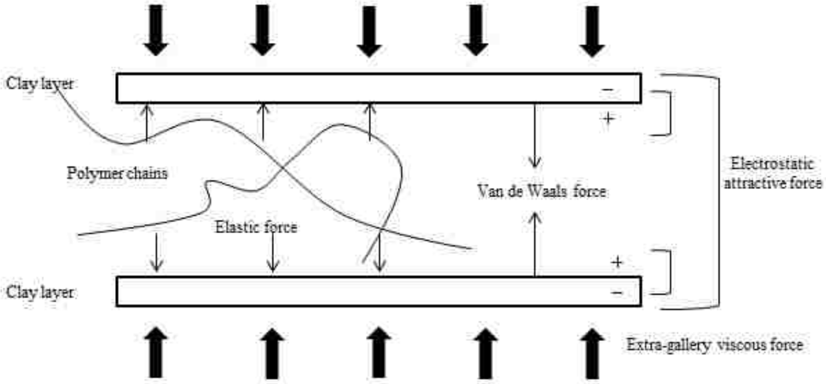


Figure 7. Schematic illustration of force acting on a pair clay layers during interaction. [162]

Few open articles have been reported for clay modified polyacrylamides used as drilling fluid in polymer flooding, however a plenty of crosslinked hybrid gels have been used as gel treatment in profile control. Y. Mansoori et al.[165] did grafting of polyacrylamide onto organophilic montmorillonite and obtain a kind of material (PCN:polyacrylamide-clay-nanocomposite) with obvious enhanced heat resistance. The glass transition temperature increased dramatically from 117.0°C (pure PAM) to 178.0°C for PCN modified with 7wt.-% clay. This hybrid idea may also be applied in synthesizing polymers for EOR to increase the heat tolerance of displacing fluid. By contrast with clay, inorganic particles were tried as modifier to design polymers as drilling fluid.

David Portehault et al. synthesized copolymer polyacrylamide-co-poly(sodium acrylate)-g-poly N-isopropylacrylamide hybrideing with hydrophilic silica nanoparticles and investigated the interactions between the polymer chains and inorganic nanoparticles.[166, 167] They found the poly N-isopropylacrylamide (PNIPA) per-se strongly interacts with silica surface, adsorbing irreversibly on the particles under low temperature, and this affinity decreased sharply to phase separate upon heating. After grafted to the poly(acrylamide-sodium acrylate), PNIPA worked as side chains still preserved their affinity for silica forming responsible bridges among polymer chains and inorganic nanoparticles and establishing hybrid networks when enough silica added into copolymer solution. Based their achievements, Dingwei Zhu et al.[102] prepared similar system for drilling fluids of EOR and investigated their properties both in pure water and brine. They pointed out that at lower polymer concentration (< CAC), less hybriding interaction occured due to aggregation; when polymer concentration reached to CMC, silica nanoparticles acted as physical crosslinkers among the entangled polymer chain, owing to attraction between carbonyl groups in HAPAM and silanol groups at the surface of nanoparticles; at higher polymer concentration (> CAC), minor enhancement in viscosity id observed. This hybriding polymer had better thermal stability than pure HAPAM. The viscosity retention ratio of the hybrid is 43%, compared to 17.47% of pure HAPAM at $85^{o}C$ for 60 days.

In the Athabasca area of Alberta, Canada, oil sand ores are low grade with high concentration of mineral solids, chemical aids are often needed in bitumen extraction. Hihong Li et al.[168] employed hybrid $Al(OH)_3$-polyacrylamide (Al-PAM)[169, 170] combing with a partially hydrolyzed polyacrylamide (HPAM) to process a low-grade oil sand ore. It appeared that Al-PAM could enhance fine clay flocculation and be capable to improve both bitumen froth quality, tailings settling and bitumen recovery.[171] For the synthesis process, they firstly prepared $Al(OH)_3$ colloidal with uniform size through $2AlCl_3+3(HN_4)_2CO_3+3H_2O=2Al(OH)_3+6(NH_4)Cl+3CO_2$ under strong agitation, then polymerized acrylamide monomers in Al(OH)3 colloidal with $(NH_4)_2S_2O_8$-$NaHSO_3$ as an initiator. Hybrid polymer was acquired after washing filtration and vacuum dry.

Although the research in these areas appears promising, few open practical applications of HAPA have yet to be published due to synthetic limitations, e.g., in product-control engineering and high chemical/product cost.

3. Cross-linked Polymer Used in Gel Treatment

Excess water production is a frequent problem occurs in mature reservoirs owing to long term water flooding. It can cause multiple concern in environment, exacerbating the levels of corrosion and scale.[172] Gel treatment normally is one of the best option for this problem.[173-175] Crosslinking polymers have been widely applied to correct reservoir heterogeneity and improve the sweep efficiency of displacing fluids (normally, water.) Gel injection can reduce flow capacity fractures and divert following fluid. The polymers mentioned in polymer flooding part have employed various cross-linkers to form gels. A polymer gel is a 3D network and can be used to obstruct higher permeability zones/streaks/channels in reservoirs so that the flowing water can enter oil-riched non-swept zones/areas to displace more oil from the formation pores.[176-184] There are many reactive inorganic and organic “functional” groups that can provide crosslinking in HPAM polymers, such as $–COO^-$, $-CONH_2$, and -COOH. Cross-linkers can also be introduced into HPAM by co-polymerizations with AM monomer. There are essentially three types of crosslinking structures employed in EOR, associative crosslinking by ionic bonds, associative crosslinking by a chelation effect, and direct crosslinking by covalent bonding.[185]

Polyacrylamide per-se is electrically neutral and comprises a saturated hydrocarbon (C-C) backbone with amide side chain groups. When subjected to aqueous alkalinity or elevated temperatures, some of the amide groups in PAM are converted to carboxylate groups where the degree of hydrolysis typically varies from 0 to 50%[15, 186, 187] The formed anionic charges can develop ionic bonding arrangement in the presence of multivalent cations[188-191] (valence state), such as B(III), Cr(III), Al(III), Zr(IV), Fe(III), or Ti(IV). Through the interaction between –COO $^-$ in PAM and one, or more, multivalent inorganic cations, a 3-dimensionalnetwork structure of the PAM polymers (see Figure 8) is achieved.[161, 192-197] Cross-linkers of this kind are inorganic, formal ionic salts but can be reduced in their effectiveness of solution viscosity control by the presence of monovalent captions such as sodium or potassium, which compete for anion association sites.

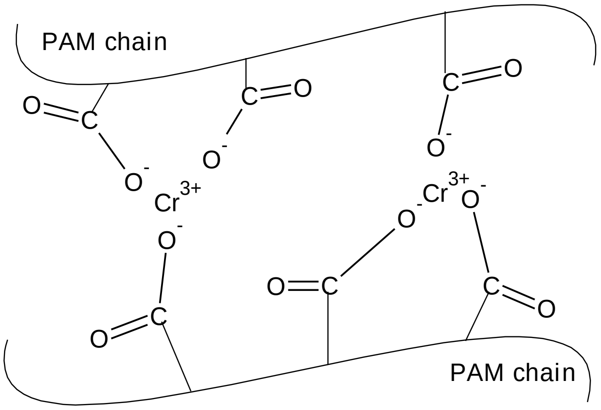


Figure 8. The sketch of a cross-linked network formation by ionic bonds using the multivalent ion Cr (III) as example.

Alternatively, multivalent metal cations of Cr (III), Al(III), Zr(IV), Fe(III), or Ti(IV) and similar cations can serve as the central ion of a chelation complex.[198] The inorganic salts of these ions are capable of forming polynuclear olation and coordinate covalent complex ions, which can coordinate and crosslink with carboxyl and acylamino groups of partially hydrolyzed PAM. Chelation cross-linked gels have the potential to develop bulk gels with higher strengths and reduced sensitivities to monovalent ions.

Additionally, to improve the material properties by introducing clay and several inorganic is a hot pot in the progress of material science recently. To make hybrid polyacrylamide with higher mechanical property, temperature and salt resistance becomes a target in gel treatment. Direct covalent bond networks can be formed by reacting the –$CONH_2$ in PAM chains through dehydration. Covalent crosslinking monomer molecules must then contain an functional group equivalence of at least two, such as formaldehyde (see Figure 9), multifunctional phenolic compounds,[199-201] phenol-formaldehyde resin,[202-204] urea-formaldehyde resins,[205, 206] and malondialdehyde, etc. These gels have higher thermal and oxidative resistance due to the increased stability of the covalent bond in comparison to associative bonding arrangements.

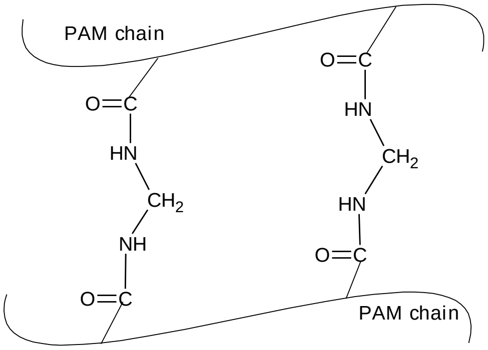


Figure 9. Sketch of a cross-linked network structure formed by covalent bonds using formaldehyde as example.

Organic crosslinking can also be obtained by copolymerization with multifunctional organic monomers, i.e., with more than a single C=C double bond, such as polyethylene glycol diacrylate (see Figure 10),[180] polyethylene glycol dimethacrylate, polypropylene glycol diacrylate, ethyleneglycol diacrylate, trimethylolpropane trimethacrylate, ethoxylated trimethylolpropane triacrylate, ethoxylated pentaerythritol tetraacrylate,N,N'-methylenebisacrylamide[207] and analogous derivatives.[208, 209] The multiple telechelic double bonds make them be capable to react with the AM monomer and participates the radical polymerization in more than one growing polymer chain resulting in the oligomer forming a crosslink between two growing chains and, overall, a network structure. Recently, micro-gels as products have been applied in the EOR field and cross-linkers appear to be mostly this type.[209, 210]

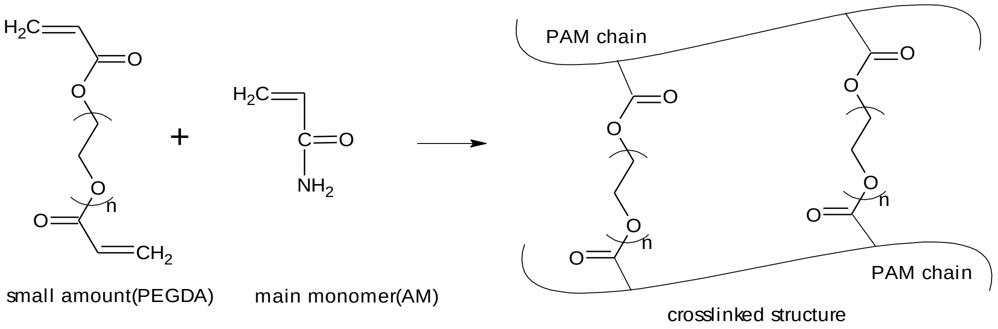


Figure 10. Mechanism of cross-linked network formation by the copolymerization of PAM withα,ω-poly (ethylene glycol) diacrylate as example.

According to the different cross-linker structures employed, there are inorganic cross-linked PAM gels (metal ions, clay and nano-powder), and organically cross-linked PAM gels. Yet, some researchers have also used both organic and inorganic crosslinking even added inorganic powder to achieve gelations of better temperature and salinity resistance.[198, 211]

3.1 Metal ion Crosslinked (Ionomer) Polyacrlamide Gels

In 1974, Needham[212] first reported to use the gel made by crosslinking HPAM with aluminum citrate to control injection profile. After that the demonstration, a series of ionomer gel systems were developed and widely used in EOR, which have achieved great success. In aluminum citrate/HPAM gelling systems, the citrate acid root protects the Al(III), preventing it from hydrolytic conversion into $Al(OH)_3$. Meanwhile, PAM can still form complex structures with Al(III) as the Al(III) is released gradually. One problem with this gel is their gelation rate is quite fast so that it cannot penetrate into the in-depth of a reservoir. Another drawback of this system is that other multivalent ions can lead to Al(III)/polymer precipitation. Advantages of this kind of gelling system include high temperature resistance, as high as 90 ℃.[213]

In the 1990s, Smith, et al.[214-217] introduced the Colloidal Dispersion Gels (CDG) system comprising HAPAM/aluminum cirate. They pointed that CDGs provided in-depth control of permeability variation by being sufficiently slow gelation to allow it deep placement in the formation.[218] When the polymer concentration exceeds acritical concentration C^* intermolecular crosslinking can occur in one or between several polymer chains. Meanwhile, the total molecular weight of the complexes grows as crosslinking increases ensuing with forming infinite networks between polymer-metal ion via complexation.[219]

The aggregates form colloidal dispersions that remain stable but may grow in size depending on the concentration of metal ion and polymer.[220] Bjørsvik, et al.[195] reported a CDG solution formed by crosslinking HPAM with aluminum as aluminum citrate.[217] In water, the system took more than 10 days to gel whereupon the gel showed less shear dependency compared to the HPAM polymer solution. In salt water, 5 wt.-% NaCl or synthetic seawater, the aluminum could bind to the polymer immediately mainly through forming intra-molecular bonds but completed gelation occurred over several days. The best ratios between polymer and aluminum were in the range of 20:1 to 100:1. Once the CDG units formed, the gel remained stable over 23 days under 60 ℃. Several field applications have been conducted with varied degrees of success.[218, 221-224] Spildo et al. screened the CDG in North Sea reservoir and significant increase in oil recovery resulting CDG injection was found. 40% of the remaining oil after water flooding was produced by CDG injection averagely.[225]

A Cr(VI)/HPAM gel system was employed in 1980’s.[226-229] Two main systems include polymer/reducing agent system and a polymer/organic chrome complex. Southard[227] pointed that dichromate could react with the reducing agent and form active Cr(III). Through developing ionic bonds, gelation was produced. In this system, the gelation rate could be well-controlled, ranging from minutes to weeks[192] since gelation rate depends on the rate of redox reaction, which is beneficial to profile control.[36] Additionally, the polymer/reducing agent system could be used in reservoir temperatures as high as 66 ℃.But due to serious carcinogenic, poisonous, and teratogenic concerns for Cr(VI),interest in Cr(VI) has given way to a focus on Cr (III)[230-238] since lower solubility renders the lower valent chromium III ion less toxic.

Xiangguo, et al.[239] studied the reaction mechanisms and properties of a HPAMs/Cr(III) system. They found crosslinking primarily occurs between different chains of the same HPAM molecule under high salinity and low concentration HPAM and Cr(III) and a network structure could be formed. Meanwhile, the viscoelasticity, resistance factor, and residual resistance factor increased which showed the cross-linked polymer solution to be strongly capable to divert the sequentially injected water/polymer flood from high-permeability zones to lower permeability zones and thus sweep more oil from an oil reservoir.

Sorbie and Seright[240] pointed out that increasing temperature would decrease the gelation period and gelling time would shorten as the salinity increased in PAM/ Cr (III) systems. The experiment was conducted in an unconsolidated columnar sand pack, which showed that the size of gelatum increased with time, which meant the apparent viscosity also increased as a function of gelation time. Sydansk, et al.[192] prepared a gelling system using Cr(III) and HPAM with formation water containing $H_2S$and the gel could remain stable at 124 ℃ for 1.5 years. Limited testing results indicated the gel formulations were able to withstand high temperatures up to 127 ℃.

The Cr(III)/HPAM system has been applied in various reservoirs and achieved great success in oilfield applications.[198, 204, 241-253] In 1990’s, the Phillips Petroleum Company launched a series of profile-control and water-shut off agents. Marathon Petroleum Company also rolled out polymer/Cr (III) systems and weak gelation system[254] where it was put into application in over 50 wells in Rangely oil field and brought improved EOR efficiency and economic benefits.[10, 255]

Considering the environmental effects of chromium cross-linkers, zirconium (IV) and titanium (IV) complexes were evaluated as alternative cross-linkers for gelation of polyacrylamide.[256] These were also able to produce stable gels in high salinity brines.[196]

3.2 Organically Cross-linked Polyacrylamide Gels

The most popular HPAM/organic cross-linker system is based on the condensation reaction between phenol and formaldehyde.[200, 257] Chang, et al.[199] synthesized gels based on a cross-linking reaction between polyacrylamide, and phenolic compounds, e.g., phenol resorcinol, and formaldehyde. This system was patented by Pfizer with the trade name Floperm 325^{TM} and the polymer concentration was typically in the range of 10,000 to 20,000 ppm.[204] Flowperm 325^{TM} gelation occurred at pH greater than 9 and the gel temperature sensitivity limit was about 149 ℃ (300 ℉) or more when using a combination of other polymers, such as phenol/formaldehyde and phenol/formaldehyde/chromium(III) crosslinking system.[258] Seright, et al.[259] and Zhuang, et al.[260] both confirmed that the gelation time of this system was very sensitive to salinity and that gelation did not occur when pH was below 7.5. A sulfomethylated resorcinol-formaldehyde (SMRF) system was then developed to improve the salinity tolerance and pH sensitivity.[261, 262]

Albonico,et al.[203] presented a phenol-formaldehyde cross-linked polymer gel system. The investigators chose low molecular weight HPAM, co-polymeric PAM-AMPS and terpolymeric acrylamide/N-vinyl pyrrolidone/acrylamide-3-propane sulfonic acid (PAM-VP-AMPS) as test samples using phenol-formaldehyde as the cross-linker.

Their results showed that the phenol and formaldehyde gelation system can withstand temperature as high as 120 ℃. In slim-tube experiments (Slim tube tests are performed to observe actual solvent-oil interaction in a physical simulation of reservoir pore space.), these gelants possessed excellent injectivity under 140 ℃. Slim tube tests are performed to observe actual solvent-oil interaction in a physical simulation of reservoir pore space.[263] Hutchins et al.[258] also showed the phenol-formaldehyde cross-linked gelling system could remain stable in oxygen-free seawater at 150 ℃ (300 ℉) for 12 months and 177 ℃ (350 ℉) for five months. With a goal of longer delay time for gelation to prevent gelation before the reactants have reached the elevated temperature target zones, Huchins et al.[258] reported an organic crosslinking system comprising HPAM and a crosslinking combination of hydroquinone (HQ) and hexamethylenetetramine (HMTA). The gel was stable for 12 months at 149 ℃ (300 ℉) and 5 months at 177 ℃ (350 ℉).

Dovan, et al.[264] described another crosslinking system that can be applied at higher temperatures featuring new cross-linkers, HMTA, terephthaldehyde, terephthalic acid, and glutaric acid as primary cross-linkers and HQ, dihydroxynaphthalene, and gallic acid as secondary cross-linkers. The primary cross-linkers were chemical compounds that can form unstable gel networks with HAPAM polymer (Hydrophobically Associative Polyacrylamide), while the secondary cross-linkers could stabilize the gels formed by the primary cross-linkers at high temperature. This system has a gelation time of several days at 168 ℃, but has not yet been tested in a field application. Due to environmental concerns, the use of HQ and formaldehyde are discouraged.

Polyethyleneimine (PEI) was also an organic cross-linker utilized to make thermally stable PAM copolymer gels.[245, 265] Morgan, et al.[266] reported a gel system based on acrylamide/t-butyl acrylate copolymer (PAtBA) cross-linked with PEI. The PEI crosslinking system was shown capable of propagating eight times farther than chromium-based systems under equivalent conditions because the crosslinking reaction is dependent on a nucleophillic attack by amine nitrogen from PEI at the carbonyl carbons of the t-butyl acrylate. Unlike many metal-based ionomer cross-linkers, PEI is not susceptible to hydrolysis.[245] Al-Muntasheri, et al.[267, 268] performed a series experiments to test PEI/PAM-AtBA gels under high temperature and pressure. The reaction mechanism is showed in Figure 11. They first reported the possibility of crosslinking PAM with PEI at temperatures up to 140 ℃ (285 ℉) and pressures up to 30 bar (435psi). In bulk, the gels were stable up to130 ℃ (194 ℉) for at least 8 weeks. At the same temperature but 69 bar (1000psi) pressure, the PEI gel was stable for 3 weeks. The PEI/PAM-AtBA copolymer crosslinking system has also been proven successful in controlling water production over a temperature range from 27 to 177 ℃ (80 ℉ to 350 ℉).[265]

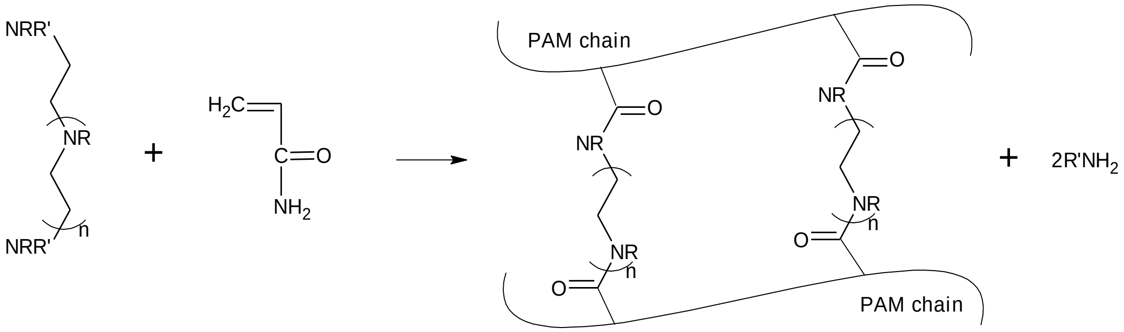


Figure 11. The Reaction Mechanism Between PAM and PEI. [267]

Baojun Bai, et al. reported a series of preformed particle gel (PPG) which is a particle superabsorbent cross-linked polymer gel.[179-184] It can swell up to 200 times its original size and showed elastic deformation ability. The strength and swelling capacity of it is controllable by adding different amount of crosslinker and other addictive agent. It is not sensitive to reservoir minerals and formation water salinity. This cut particle gel with certain size comes from bulk gel synthesized in solution with methylene-bis-acrylamide (MBAM) as crosslinker, one or several of acrylamide, acrylic acid, 2-acrylamido-2methylpropane sulfonic acid and other vinyl functional monomers as co-monomers. The organic cross-linkers with multiple telechelic double bonds were employed to realize 3-D gelation structure. After dried, cut or crushed, the particle gel was produced from a bulk of large gel.[179, 269] When blocked by rocks in reservoir, it can go through the fracture via deformation. Yet the salinity can decrease the swell property of this gel, it can promote its strength. Furthermore, some PPGs perform stable under as high temperature as 120℃.[177, 180, 181] PPG treatment has been applied in four injection wells located in the north lF Lamadian, Daqing oilfield, China, which is sandstone oilfield with thick net zones. PPG suspension with concentrations of 2000-2500 mg/L and particle sizes of 0.06-3.0mm was injected into reservoir (water cut of 95.4% before treatment). This resulted in an oil increase of 34.8t/day and average water cut decrease of 0.94% within 10 months after treatments.[182] So far, the PPGs have been used successfully as conformance control agents in more than 5000 wells to help control both water and CO_2 production.[182, 183, 270] Transport mechanism through porous media of PPG was investigated from microscopic and macroscopic scale.[181, 184] Other evaluation information can be reviewed in other lab test.[271, 272]

Based on the solid background of PPG, Bai proposed a kind of thermo-dissoluble polyacrylamide (TDP) crosslinked gel which can be used for in-depth-mobility control.[273] TDP was prepared in solution free radical polymerization and two crosslinkers were adopted to control the strength and effective time, N,N'-methylenebisacrylamide (MBAA) worked as stable crosslinker, and polyethylene glycol diacrylate (PEGDA) served as the weak one. After drying and cutting, bulk gel were crushed into particle gel. This particle gels were firstly injected into the fractures or kind of features acting as plugging agent and then dissolves into polymer solution at a designated time stimulated by reservoir temperature. The formed polymer solution then seeped into the depth and behaved as a mobility control agent.

Zhou et al.[274] developed a plugging agent employing KYPAM and polyethyleneimine through a crosslinking reaction between –NH–of $(–CH_2\text{-}CH_2\text{-}NH–)_n$ and the $–CONH_2$ of KYPAM (see Figure 12). The resulting polymer had a molecular weight of $8x10^6$ Da that can be used in reservoir temperatures from to 80 to 110 ℃ and salinity ≤80g/L NaCl + 1.2g/L $CaCl_2$. Additionally, the KYPAM cross-linked polymer

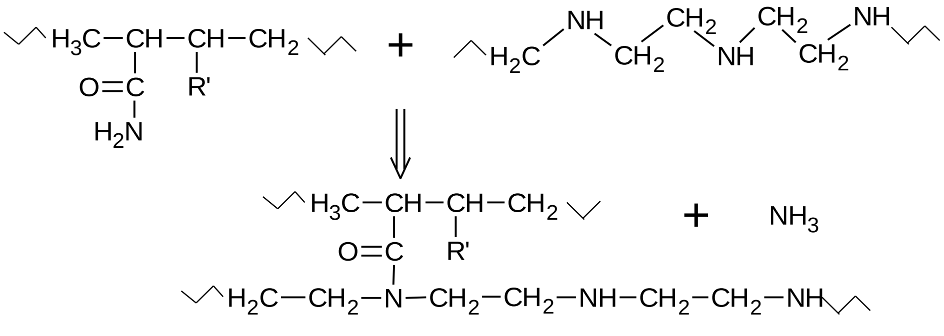


Figure 12. Mechanism of KYPAM-PEI crosslinking gelation reaction.

has higher threshold pressure and strength and stronger washing resistance than phenolic/KYPAM plugging agents.

Due to cost and performance considerations, PEI has found use in forming gels with mixtures of AM, AMPS and N,N-dimethyl acrylamideco-polymers [275] as well as simple PAM.[276] PEI-based gel systems have been used in various water shut-off lab evaluation where it has found good success.[245, 265, 277-287] Hardy[288] has described a co-polymers (PAtBA) of acrylamide and t-butyl acrylate, using PEI as the cross-linker. He used the gel in Ekofisk oilfield, Norwegian Sector of the North Sea. For the treatment, the 7%PAtBA was mixed in the platform injection water tanks first, then the PEI was blended with the polymer solution, finally pumped the mixture down hole through coil tubing with the injection rate at 12.58m^3/min. The detailed results are in Table 2.

Table 2
Production of the B-21A Well: Immediately before and after the organic crosslinking polymer treatment.[288]

Interval	Pre-Job	Post-Job
10715 to 10720 ft	27.6%	16.67%
10760 to 10765 ft	13.8%	12.5%
10808 to 10813 ft	13.8%	12.5%
10855 to 10865 ft	20.7%	26.25%
10904 to 10914 ft	13.8%	15.41%
10953 to 10963 ft	10.35%	0%
11003 to 11013 ft	UNK[a]	16.67%
11040 to 11045 ft	UNK[a]	UNK[b]
11053 to 11063 ft	UNK[a] UNK[b]	UNK[b]
11185 to 11195 ft	0%[b]	UNK[b]

a. Not accessible to the logging tool due to the obstruction.
b. Assumed to be 0% due to the CaCO3/cement plug.

The technology using organic cross-linker is considered mature and many field application examples of organically cross-linked PAM flooding polymers can be found.[258, 286, 288, 289]

3.3 Polyacrylamide Micro-gels/Micro-spheres

PAM micro-gels are, in general, also cross-linked by organic cross-linkers. Micro-gels are special colloidal gel particles or polymers, which have been shown to be able to change their gel configuration in response to external stimuli.[290] Unlike macro-gels, micro-gel or sub-micro-gels have been designed to activate certain properties at a pre-determined “in-depth” location within in the reservoir (see Figure 13). For instance, micro-gel systems typically contain expandable polymeric particles possessing both labile and stable cross-linkers. Under the stimuli of pH or temperature extremes, the labile cross-linker will degrade to decrease the degree of crosslinking where the polymeric particles can expand to many times their original volumnar size (see Figure 14), which can block pore throats and direct injection water into unswept oil-rich zones. Inverse-emulsion, micro-emulsion, suspension, and precipitation polymerization methods are the most common approaches to establish control the particle sizes within a narrow range, from milli- to nanometer size scales.

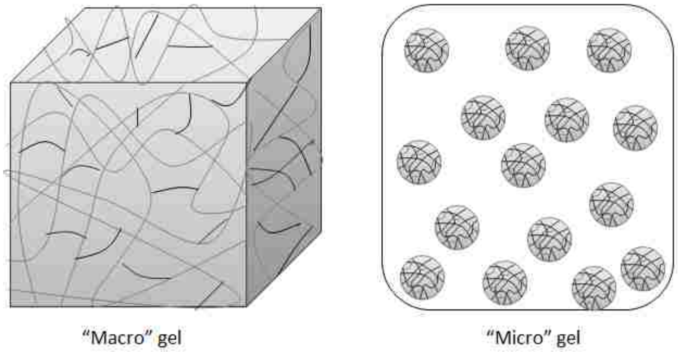


Figure 13. Illustration of the fundamental difference between macro-gels and micro-gels. [291]

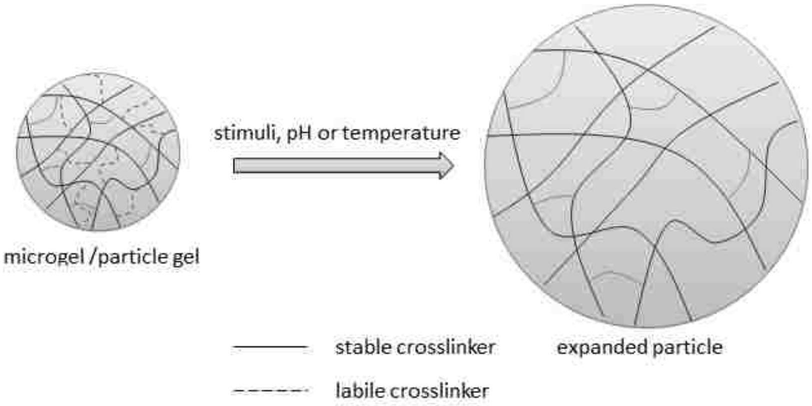


Figure 14. Proposed swelling mechanism of an expandable polymer particle.

An example of a micro-gel joint research and development by an industry consortium (BP, Chevron Texaco, and Nalco Company) was called the Bright Water project. The micro-gel product has been in practical application since 2001 and has been applied in about 60 wells. In preparation of the product, the initial polymeric "kernel" particles sizes of 0.1 to 3 um were first synthesized through an inverse emulsion polymerization process.[292-296] Through esterification between carboxylic and hydroxyl groups under an azeotropic, thin film evaporation technique to remove water, the polymeric micro particles were internally cross-linked with labile cros-slinker. Upon adding light mineral oil, surfactants, brine, and completely mixing, a dispersed kernel particle suspension was obtained, without aggregation, in brine.

The suspension contained particles within a 0.5 to 1 micron size range, which easily pass through the reservoir channel. When the micro-gel particles reached the desired location, decomposition of the labile cross-linker in the kernel particles lead to particle absorption of water and volume expansion. Furthermore, the particles were observed to interact with each other on a larger scale that was from 10 to 30 times larger than the original single particle size.[297] In high permeability, porous media, the micro-gel could be enhanced by increasing micro-gel concentration.[298]

Ensuing after the successful application of Bright Water, many similar swellable polymers or DDG[207-209, 299-301] were developed. For example, Moradi-Araghi et al.[302] invented stable, cross-linked water-soluble swollen polymers comprising expandable micro polymer particles using labile, water soluble diacrylates, such as PEG200 diacrylate, crosslinking agents, stable crosslinking agent monomers, e.g., methylene bisacrylamide, and a tertiary cross-linker such as formaldehyde or hexamethylenetetramine that can become activated once the labile cross-linker degrades under pH or temperature. The micro-gel system could be capable of being further cross-linked to form an expanded and stable gel. The polymer particles were prepared from AM and AMPS through inverse-emulsion polymerization where the particles were co-cross-linked with methylene bis-acrylamide as the stable cross-linker and either PEG-200 or PEG-400 diacrylate as the labile cross-linker.

There are several advantages to conducting acrylamide polymerizations by the inverse emulsion process. However, with these advantages there are also several disadvantages, including the presence of oil and the eventual phase separation of the oil for inherently unstable emulsions. The oil is also an undesirable field contaminant in most applications. Therefore, the oil is typically removed post-polymerization, replaced by an alternative oil phase, or simply emulsified with the micro-gel dispersion during the field application.

Potential problems associated with the oil phase may be bypassed by carrying out the reaction in supercritical gas fluids, from which powdered products can be obtained directly. Supercritical fluids offer advantages in that they exhibit “liquid-like” densities and solvency power while having “gas-like” viscosities.[303] Currently, many polar or hydrophilic molecules, such as water, proteins, amides, ionic species, sugars, etc., exhibit very poor solubility in supercritical carbon dioxide ($ScCO_2$)and only limited research efforts have been made towards polymerization of water-soluble vinylic monomers containing amides in $ScCO_2$, including inverse emulsion polymerization of acrylamide,[304] polymerization of N-ethylacrylamide, and dispersion copolymerization of N,N-dimethylacrylamide.[305]

Inverse-emulsion polymerization in $ScCO_2$ requires that the monomer be relatively insoluble in $ScCO_2$. Adamsky et al.[304] reported the inverse-emulsion polymerization of AM monomer in $ScCO_2$. The key point for the emulsion polymerization was to choose the proper emulsifying agent. Adamsky et al. synthesized an emulsifier with a carbon dioxide compatible, fluorine and also amido groups. (see

Figure 15) By virtue of the CO_2-soluble amphiphiles, acrylamide was successfully polymerized using inverse-emulsion polymerization in $ScCO_2$.

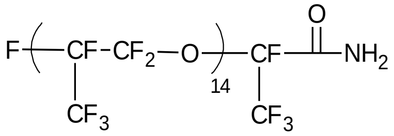


Figure 15. The surfactant of inverse-emulsion polymerization of acrylamide in $ScCO_2$. [304]

Ohde et al.[303] synthesized polyacrylamide nanoparticles by inverse emulsion polymerization in $ScCO_2$. The chosen surfactant was a perfluoropolyether-phosphate and the initiator was potassium persulfate. Through the inverse emulsion method, the nanoparticles were obtained with a size distribution between 50 and 200 nm.

Table 3
The change of injection characteristic parameters before and after the polymer microsphere treatment.[306]

	Before			**After**		
Well	Wellhead Pressure (MPa)	Pressure index (MPa)	Fill degree(%)	Wellhead Pressure (MPa)	Pressure index (MPa)	Filling degree (%)
A09	7.0	0.67	10	8.3	5.15	1.5
B14	4.9	1.37	35	8.0	5.05	1.4
C05	1.0	0.12	12	6.4	4.80	2.8
C21	1.1	0.21	21	6.2	4.63	2.7

Liu et al.[306] presented an oilfield application of polymer microspheres flooding in reservoir Q in Bohai Bay, China, which was a heterogeneous heavy oil reservoir suffering from fast water breakthrough with poor recovery. The pilot tests were done in four wells. Three types of polymer microsphere were used with the concentration of 5000, 3000, and 5000mg/L, and injection pore volume of 0.01PV, 0.005PV and 0.015PV. Good pore occlusion was observed, as shown in Table 3. Injection pressure, pressure index and filling degrees were greatly raised. Filling degree refers to measure the sealing pore volume and the unsealing pore volume. Additionally, the oil production decline rate was reduced from 7.0% to 4.9%, and water cut was reduced by 2.8% on average.

Crosslinking polymer systems based on multiple cross-linkers were also adopted due to desire of multiple properties.[254, 283, 307]

3.4 Polyacrylamide Gels Modified by Combined Crosslinker and Hybrid Polyacrlamide Gels

Heterosis or hybrid vigour is a concept widely used in genetic engineering to cross breeding for better strains[308] and it’s also applied in material engineering. Modifying the material with combing elements, may give us new ones carrying the complex advantage sometimes. Current PAM gels used in preform control are mainly made by both organic and metal ionic crosslinkers. Furthermore, various clay and inorganic nanoparticles are also incorporated for our use to promote the mechanical properties, heat resistance, salt resistance of the PAM gels[172] or bring special effects,[309] for example, some nano-particles have been shown to stabilize foams and emulsions or change the wettability of rock,[310] and the incorporation of inorganic elements can modify the surface properties of the gels.

Reihaneh Zolfaghari et al.[161] reported a nanocomposite hydrogels made by crosslinking the polyacrylamide/montmorillonite (Na-MMT) clay aqueous solution with chromium (III). Interactions exist as ionic force between polymer chains and chromium (III); gallery viscous force between polymer chains and clay; and hydrogen bonding. Multiple effect produce better strength. This kind of gel showed more rubbery behavior with higher extensibility and deformability thereby it has better pressure resistance during EOR after being developed in reservoir.

Samira Abdolbaghi et al.[45] published a method to prepare polyacrylamide/nanoclay hybrid nanoparticles via inverse Pickering emulsion polymerization in which the inorganic particles work as surfactant to stabilize the emulsion.[311-313] The W/O emulsion is obtained by adding clear dispersion containing nanoclay particles into aqueous phase (AAM, MBAM, initiator mix with water). Inverse Pickering emulsion polymerization was carried out in a three-neck flask with argon injected. AIBN/cyclohexane solution was added into the system under 50°C to initiate the reaction. The composite particles are with an average size of ~250 nm. Regrettably, the author did not mention how they deal with the low solubility of AIBN in cyclohexane along with the unstable effect due to the insolubility of the initiator. Furthermore, as is well-known, the effective decomposition temperature for AIBN is over 70°C (half-life 1.3 hours at 80°C)[314] if not in redox initiating system.

Jamal Aalaie et al.[194] prepared a kind of nanocomposite hydrogels by crosslinking of aqueous solution of sulfonated polyacrylamide/sodium montmorillonite with chromium triacetate. They made polymer solution, PAMPS solution and clay/water dispersion first, and then gradually add them together with cross-linker under heat and stirring to let reaction complete. After purification and drying, the final product was achieved. Gelation behavior indicated that the clay content enhancing lead to viscous energy dissipation properties of the nanocomposite gels increased. Identically using montmorillonite as inorganic modifier, Xudong Nie et al.[315] prepared amphoteric nanocomposite hydrogels without adding chemical crosslinking agents. This hybrid hydrogel processes great swelling capacity and compression strength of 54.4 kPa under water content of 99.8%. Paul Tongwa et al.[172] used similar method made nano composite gels without additional organic crosslinkers. They selected lapointe, a synthetic layered silicate, as modifier, which can interact with the negative charge on anionic PAMs' chains to form network structure. They observed strong polymer-clay in interaction from dense hydrogel network.

Bai did a large amount of work on hybrid PPG and its application.[172, 179-184, 269-273] Based on their former work, PPG hybriding with bentonite clay has been prepared and applied successfully to correct in-depth reservoir permeability heterogeneity in most mature oil fields in China. Case 1. PPG treat two wells in Zhongyuan oil field, SINOPEC in 1999 due to the following reasons: a, high water injectivity; b, high average water cut of more than 85% for connected production well; c, severe areal heterogeneity and channel between injectors and producer. After injected of 4300 m^3 PPG suspension (13000kg dry PPG) into Well W51-75, and 2500 m3 PPG suspension (made from 7500 kg dry PPG) into Well P-72, positive responses come out: water injection pressure of Well W51-75 increased from 16 to 19 MPa, and 19.5 to 24 MPa for Well P-72 . Moreover, the continued enhancing injection pressure after treatment last more than 2 years, indicating PPG is stable for more than 1 years under formation conditions. Case 2: The PPG treatment is in Daqing, PetroChina. Positive results were shown: a, injection pressure was increased from 5.0 to 11.6 MPa; b, areal heterogeneity was effective controlled; c, about 2400 tons of incremental oil was exploited and 8% water-cut decreased; d, the useful life of PPG is over 6 months.[180]

4. Conclusions

This paper mainly reviewed the function of polyacrylamide and its derivative products in EOR through two main aspects: one is the viscosity thickener as the polymer flooding agent; another is they can act as sealing agent via forming cross-linking structure in present of cross-linkers to render conformance control. This review clearly indicates the structure of the different polyacrylamide and their derivatives as well as the according properties of them. In particular, this review elaborates synthesis methods of each kind polymer and gives their application in detailed.

For the polyacyrlamides working as the displacing agent, they work as a basic thickening agent in polymer flooding solution. As the reservoir environment turning harsher and harsher, kinds of modification method came up aiming at resist the high temperature, high salinity, and poor pH. According to Table 4, there is a number of typically functional monomer can be employed to modify the polyacrylamide chain hence increase the solution viscosity facing different reservoir. Among the polyacrylamides, high molecular weight PAM/HPAM is of the longest history no matter in preparation or in field application. Then, through introducing hydrophobical side or ionic side, researchers found same viscosity increasing phenomenon happened in not high molecular weight PAM. A lot of research has been done in these two kinds of polyacrylamides and successful filed application can give us pragmatic instruction.

Gradually, research tried to combine both the ionic and hydrophobical modification and get some progress but less practical field application.

For the polyacrylamide effect as sealing gel, different polyacrylamides place an important part in sealing various areas with different permeability and environment conditions. Generally, large bulk gels are synthesis by solution method and using metal ion or organic cross-linker to achieve 3-D network structure. They will work to seal the large fracture or large channel so that change the direction of the flooding solution and harvest the oil from the production well. While, the large gel cannot penetrate the thief areas with tiny hole size. Hence micro-gel will work for this. Usually, micro-gel come from emulsion/micro-emulsion polymerization so that their size can be well controlled by virtue of adjusting the composition of pre-emulsion and reaction shearing rate. They can go through narrow pore and channel to reach the target site and seal it thereby rendering in-depth profile control. PPG come from cutting the bulk 3-D gel can also do this work only through fine granding Hybrid material is a promising direction in PAMs Gel preparation. It holds attractions however not too much real work has been done. Table 5 gives a summery about different kinds of cross-linkers and their properties. Selection of a given gelant greatly depends on the practical temperature, salinity, and hardness of the reservoir as well as the condition of the solutions (brine, water, or sea water).

The demanding, hostile field environments such as high temperature and high water salinity and hardness in oil recovery has required unique polymers with new structures. Polymer design developments include non-ionic monomers were more resistant to chemical alternation, and the neighboring acrylamide moieties also stabilized; anionic monomersproduced polymers that were more resistant to cation shielding and self-precipitation; hydrophobic monomersendowed intermolecular association which is favorable for efficient viscosity enhancement[316]; long polymer chains of high molecular weight were used with engineered side chains as “arms” to affect solution viscosity; high molecular weight linear PAM chains were used as a backbone to proffer hydrophobic side chains with intermolecular association effects. .Lastly, it appears that environmentally friendly methods, such as ScCO$_2$polymerizations, and EOR products should be developed whenever accessing natural resources, to be ever mindful of environmental protection.

Table 4

Summary of some typical co-monomers to modify the PAMs.

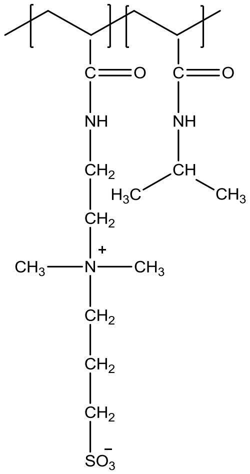
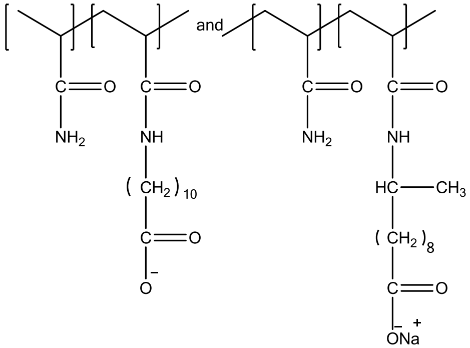
Structure	Initiator	Surfactant	Comments	Ref.
Solution polymerization				
	K2S2O8TEMED/ (N,N,N,N-tetramethylethylenediamine)		Zwitterionic sulfobetaine polymer	[68]
	(NH4)2S2O8	-	Through this method, the production is pure without surfactants.	[69]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

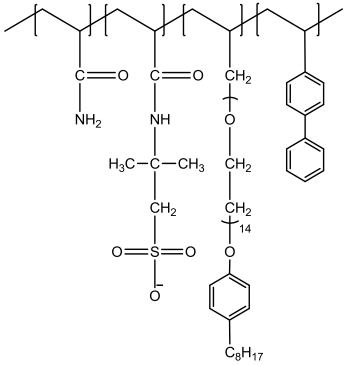
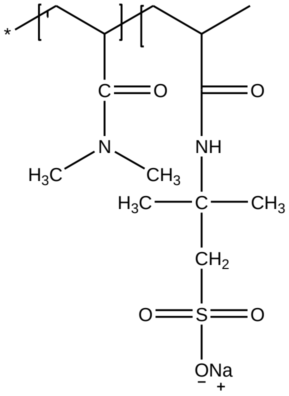
	K2S2O8	SDS	Good resistance to aging due to simultaneous incorporation of bulky side groups	[77]
	$(NH_4)_2S_2O_8$ and sodium metabisulfite	-	Thermally stable at 120 ℃ at least for a period of 1 month.	[127]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

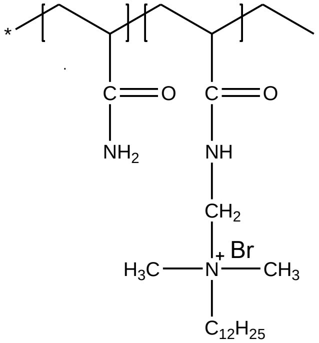
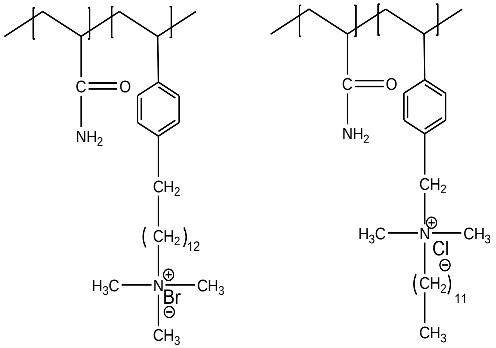
	$K_2S_2O_8$ without extra surfactant added; AIBN with extra surfactant added.	Cationic surfactant	Microblocky structures;	[34]
	AIBN	Polymerizable surfactant	Hydrophobically modified polyacrylamide	[351]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

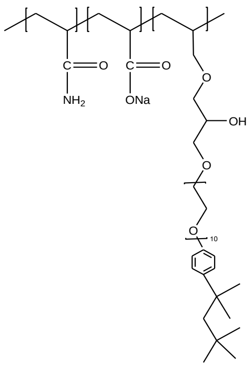
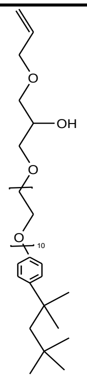
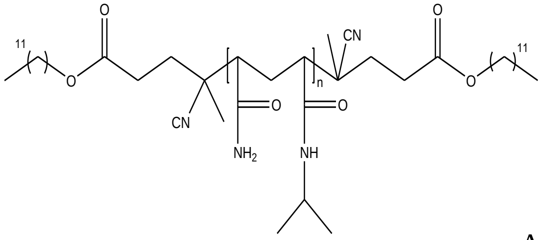
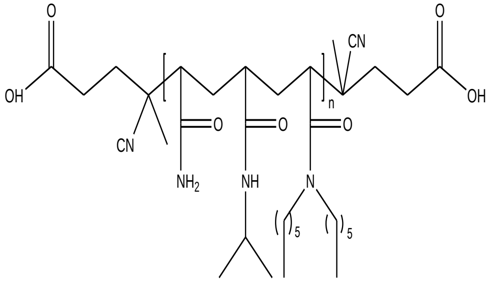
	$(NH_4)_2S_2O_8$–$NaHSO_3$		Self-polymerizable surfactant; the copolymer solution showed a good ability to emulsify organic components.	[352]
Telechelic Structure:  **Multisticker Structure:** 	Azobis(4-cyanopentanoic acid) (ACVA)	SDS	Three different types of associative watersoluble polymers were prepared by a free radical solution polymerization. (telechelic, multisticker and combined polymers)	[162]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

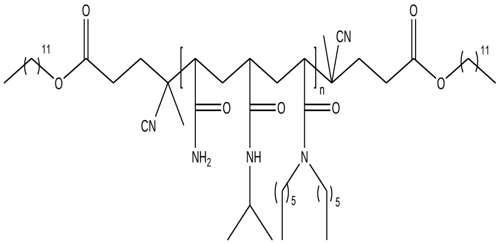
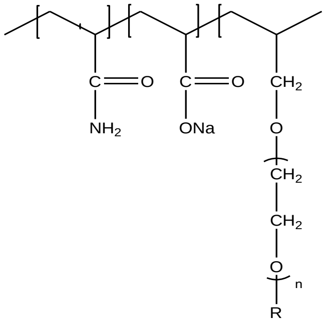
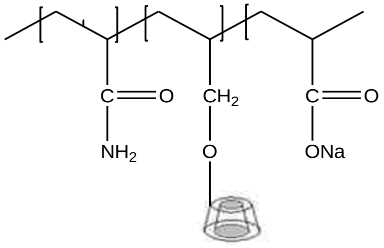
Combined structure: 				
	$K_2S_2O_8/NaHSO_3$	-	Comb-shaped	[29]
	$K_2S_2O_8/NaHSO_3$	-	Inclusion property.	[184]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

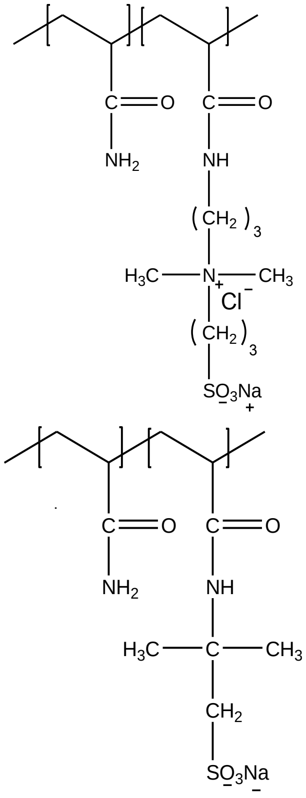
	$K_2S_2O_8$	-	zwitterionic polyacrylamide	[185]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

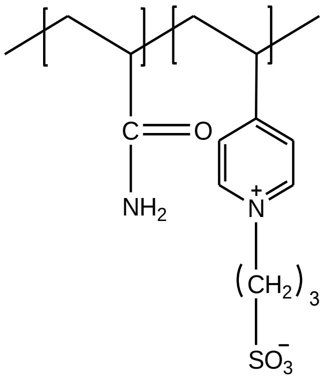
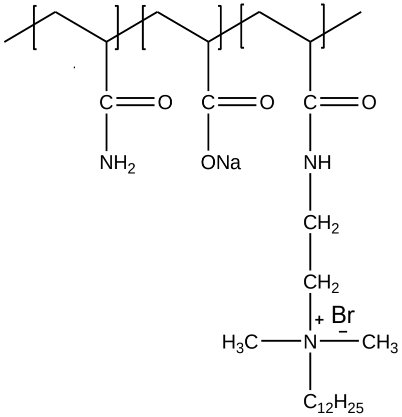
	$K_2S_2O_8$/$NaHSO_3$		zwitterionic polyacrylamide	[191]
	2,2’-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044)	-	Hydrophobically associating	[196]
PAM-Al(OH)$_3$ hybrid polymer	$(NH_4)_2S_2O_8$/$NaHSO_3$	-	Hybrid PAM	[24, 206]

Table 4
Summary of some typical co-monomers to modify the PAMs. (Cont.)

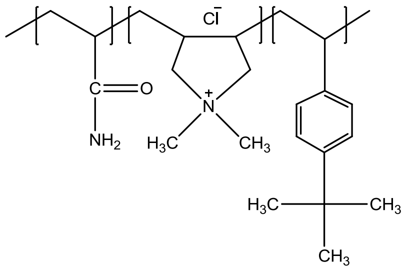
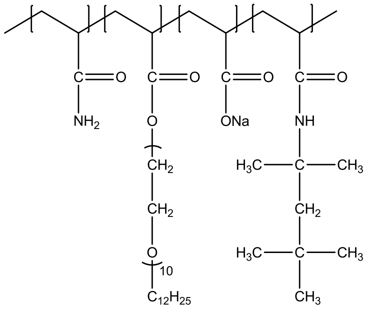
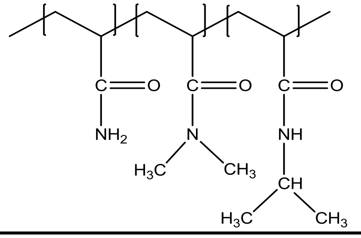
Micellar Co-Polymerizaton				
	$K_2S_2O_8$	Sodium Dodecyl Benzene Sulfonate(SDBS), cetyltrimethylammonium bromide (CTAB)	Tree-like structure will form with increasing NaCl concentration,	[70]
	$K_2S_2O_8$/ $NaHSO_3$	-	Amphiphilic polyacrylamide	[78]
	Hydrophobic Synthesized initiator with a long linear chain (C16)	SDS	Combined thermally insensitive polymer	[79]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

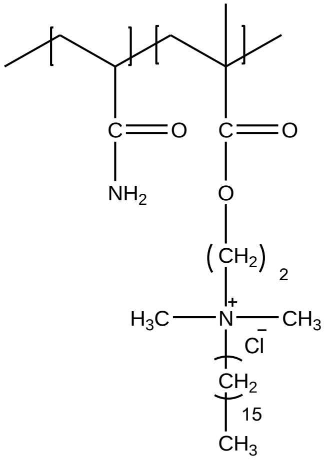
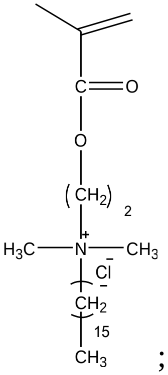
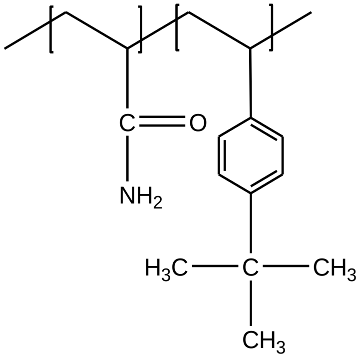
	V-50 (2,2-azobis(2-amidinopropane)dihydrochloride)	 ; SDS	Ionic modified polymer	[81]
	$K_2S_2O_8$	SDS	Hydrophobic acrylamide-modified copolymers; good anti-aging property in brine solutions at 80 ℃	[147]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

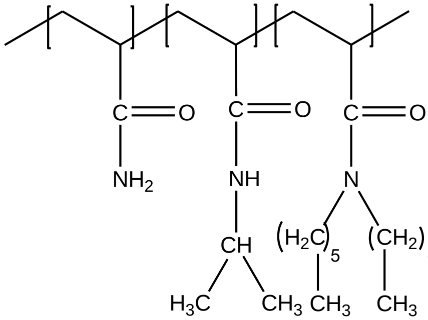
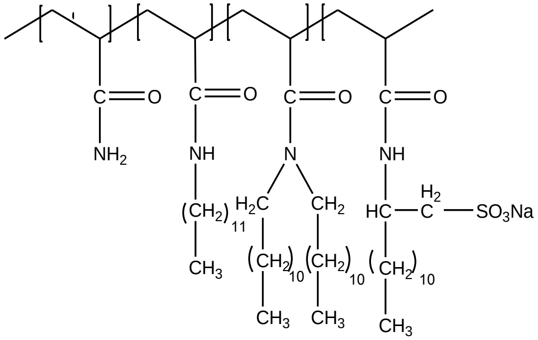
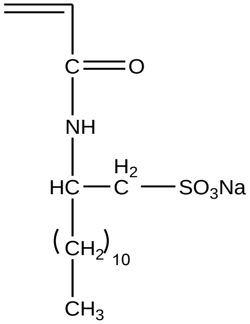
	4,4'-azobis(4-cyanopentanoic acid) (ACVA)	SDS	Thermal insensitive hydrophobically modified polyacrylamide	[213]
	$K_2S_2O_8$		Polymerizable surfactants	[159]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

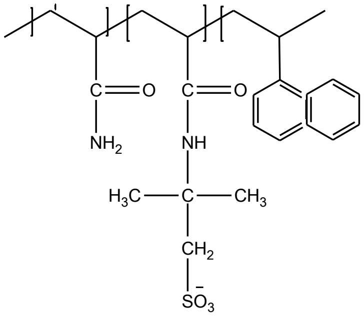
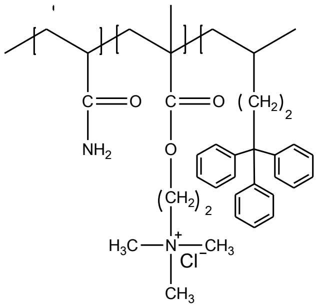
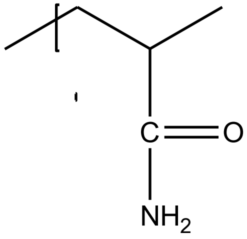
	AMPS	SDS	Hydrophobically modified polyacrylamide	[163]
	$K_2S_2O_8$	SDS	Hydrophobically associating acrylamide-modified terpolymers containing both cationic groups and hydrophobic segments cationic groups and hydrophobic segments	[164]
Inverse Emulsion Polymerization				
	AIBN, BPO, $K_2S_2O_8$	Tween85; Span 80		[84]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

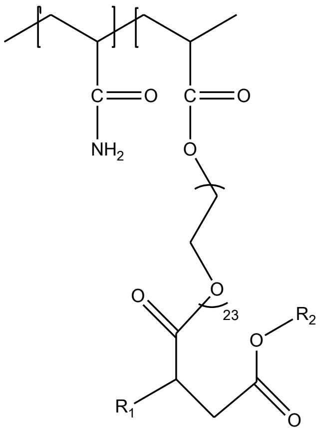
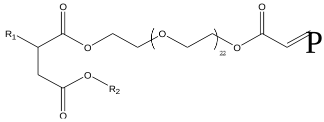
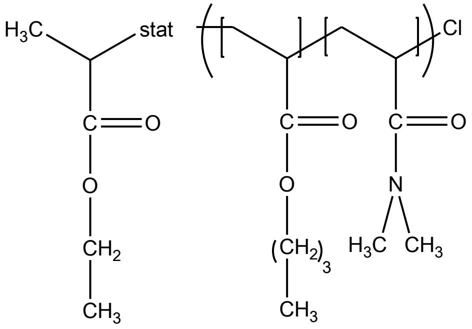
	$K_2S_2O_8/NaHSO_3$		Polymerizable surfactants	[353]
Living Polymerization				
	MeClPr/CuCl/Me_6TREN as the initiator/catalyst system	-	Hydrophobically modified polyacrylamide	[92]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

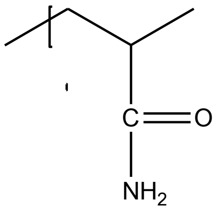
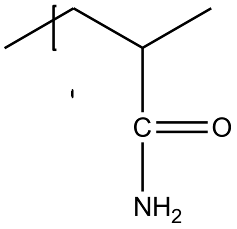
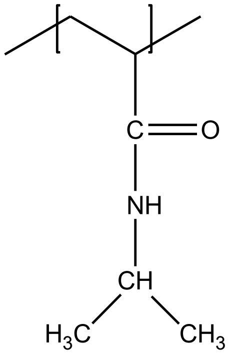
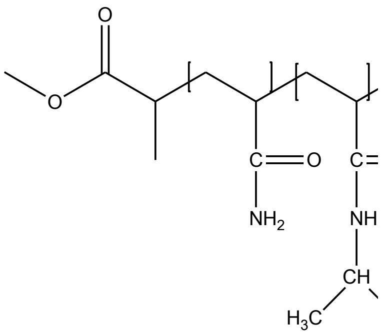
	Viz.2-chloropropionamide, (2-Cl-PA) or 2-bromopropionamide (2-Br-PA) and CuX (X) Cl, Br) bipyridine complex	-	The ATRP of acrylamide is achived achieved in glycerol-water medium at 130 °C using both Cl- and Br-based initiating system, in presence of CuX2 and alkli halides.	[93]
	Stereospecific catalyst :Lewis acid $Y(OTf)_3$ or $AlCl_3$ Initiator:chloroacetic acidAcid/CuCl/N,N,N',N' -tetramethyl ethylenediamine (TMEDA)	-	Low polydispersity index of 1.03 and high tacticity with meso content up to 76% at the optimal reaction condition.	[94]
	Macroinitiator: PAM-Cl 	-	Branched high molecular weight of PAM.	[95]

Table 4

Summary of some typical co-monomers to modify the PAMs. (Cont.)

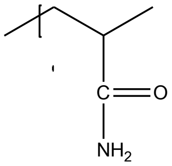
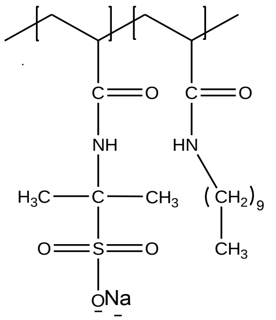
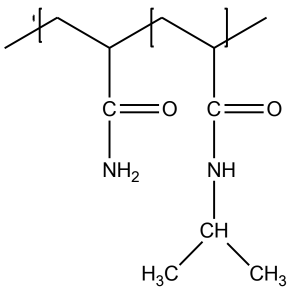
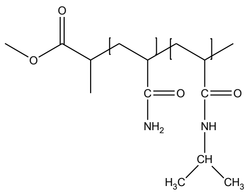
	Halogen-functionalized aliphatic polyketones			[97]
	AIBN	-	RAFT; micelle-forming, amphiphilic copolymers or “polysoaps”	
	 And (Me6TREN)/copper halogenide (CuX) as the catalyst	-	Linear PAM with apparent molecular weights up to >150 000 g/mol and dispersities as low as 1.39.	[130]

Table 5

Preparative Conditions for Cross-linked PAMs.

Monomer/Polymer	MetalIonomer Crosslinking Reagents	Initiator	Surfactant	Comments	Ref
		Solution polymerization			
N-isopropyl acrylamide (NIPAM); acrylamide (AAm); crotonic acid; itaconic acid; aconitic acid;	N,N-methylene bisacrylamide(Bis)	$(NH_4)_2S_2O_8$+ TEMED	-	Environmentally sensitive hydrogels responsive to various Stimuli such as temperature, pH, ionic strength of the medium	[76]
Polyacrylamide	N,N-methylene bisacrylamide, PEG diacrylate	-	-	Preformed particle gel(PPG)	[46, 303-306]
Polyacrylamide	N,N-methylene bisacrylamide(Bis); Bentonite clay.	Peroxide disulfate	-	Preformed particle gel(PPG)	[43, 214-218]
Alginate/polyacrylamide hydrogels	various multivalent cations, MBAA	$(NH_4)_2S_2O_8$	-		[222, 224]
Polyacrylamide	Al(III)	-	-	Colloidal dispersion gels (CDGs)	[229, 247, 250, 251, 253, 264]
partially hydrolyzed polyacrylamide/ scleroglucan	Cr(III)	-	-	Semi-interpenetrating polymer network gel	[231]

Table 5

Preparative Conditions for Cross-linked PAMs. (Cont.)

Polyacrylamide	Cr(III)-carboxylate-complex crosslinking agent	-	-	Acrylamide-polymer/Cr(lII)-carboxylate gel	[226]
Polyacrylamide	Zr (IV)				[290]
Poly-Acrylamide/N-vinyl pyrrolidone/ acrylamide-3-propane sulfonic acid (PAM-VP-AMPS) and PAM	Phenol, formaldehyde, Cr(III)	-	-		[238]
Polyacrylamide	Al (III), Cr (III), Ti (IV), Zr (IV), Fe (III)	-	-		[239]
Polyacrylamide	Cr (VI)				[261-263]
Poly-acrylate	Resorcinolformaldehyde, sulfomethylated resorcinol-formaldehyde	“Azo” activator			[294, 299]
Polyacrylamide	Polyethyleneimine (PEI)			High temperature tolerant (130 °C)	[301, 309, 315]
		Inverse Emulsion Polymerization			
Acrylamide; methylacryloxylethyl trimethyl ammonium chloride	Methylene bisacrylamide	$(NH_4)_2S_2O_8$/ $NaHSO_3$	Span80 and Tween60, SDS		[85]

Table 5

Preparative Conditions for Cross-linked PAMs. (Cont.)

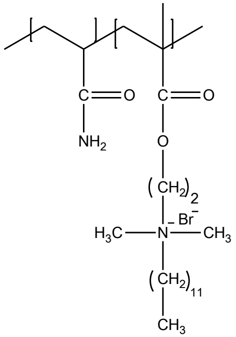
Poly-acrylamide/ acrylic acid	Attapulgite nanorods	$(NH_4)_2S_2O_8$/ $NaHSO_3$	Span 80	Hybrid microgel: Attapulgite;	[91]
Acrylamide	Methylene bisacrylamide	$K_2S_2O_8$ /$NaHSO_3$	Span 80	Swellable Microgel nanospheres	[241]
		inverse suspexnsion copolymerization; mixing			
N-isopropylacrylamide	N,N-methylene bisacrylamide	AIBN	Not provided	Nanogel	[88]
	Silica nanoparticles	(AZO Bis) 1,1′-Azobis(cyclo hexanecarbon itrile)	Not mentioned	Hydrophobically modified polyacrylamide	[144]

Table 5

Preparative Conditions for Cross-linked PAMs. (Cont.)

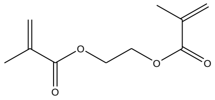
Super fluid synthesis/ Inverse emulsion polymerization					
Polyacrylamide	Intra and intermolecular imidization	$K_2S_2O_8$	Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) ; co-surfactant: perfluoropolyether-phosphate (PFPE–PO4)	Nano particle	[337]
N-isopropylacrylamide (NIPA)		AIBN	carboxylic acid end-capped perfluoropolyether oil as a stabilizer	microparticles	[339]

Table 5

Preparative Conditions for Cross-linked PAMs. (Cont.)

		Pickering emulsion polymerization			
Acrylamide;	N,N′-Methylene bisacrylamide (MBAm)	2,2′-azobis(isobutyronitrile)	hydrophobic Cloisite 20A (MMT20)	Nano particle: 250nm	[87, 346],
Poly(N-isopropylacrylamide)/poly(methyl methacrylate)/silica hybrid	reactive silanol	$(NH_4)_2S_2O_8$	silica nanoparticles		[347]

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II. Polyacrylamides and hydrophobically modified polyacrylamide by a water-free Suspension polymerization: the synthesis and characterization

Zun Chen,[1] Thomas P. Schuman[1] and Baojun Bai[2]

[1] Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65401

[2] Department of Petroleum Engineering, Missouri University of Science and Technology, Rolla, MO 65401

ABSTRACT

A water-free solvent-in-oil suspension polymerization had been developed in preparing polyacrylamides. By virtue of this method, hydrophobically modified polyacrylamide could be synthesized with polymerizable surfactant utilized, worked as both surfactant and hydrophobic commoner. The problem of incompatibility between acrylamide and hydrophobic co-monomer had been solved. The products are solid microspheres, readily separated from solvent. Compared to traditional inverse suspension/emulsion polymerization, the monomer in oil system employs less surfactant, is a less energy intensive process and solvent can be recycled. A series of poly (acrylamide-co-alkylacrylamide)s had been synthesized. The structures of the copolymers had been characterized by FTIR, NMR, TG. The mechanism of this water-free suspension polymerization had been proposed.

Keywords:

Hydrophobically Modified Polyacyrlamide; Suspension Polymerization; Associating Polyarylamide**.**

1. Introduction

Hydrophobically modified water soluble polymers are hydrophilic macromolecules containing a small fraction of hydrophobic groups which are distributed along the polymer chain or presented as end groups of the side chain.[1] The main hydrophilic domain renders solubility of the polymer chain in aqueous phase. For the lipophilic groups distributed along the polymer chain, the amount of them is small yet, they prefer to associate therefore to form physical linkages due to the unfavorable aqueous solvent conditions. These physical linkages exist both inter and intra molecular hence rendering a kind of dynamic transient network. Different from high molecular polymer, which will lose their thickening ability due to easily degradation under high shearing. For hydrophobically modified polymer, the self-assembling is reversible in nature as the hydrophobic interactions can be disrupted when subjected to high shearing, but re-form when shear is reduced. [2-6] These polymer are also regarded as self-healing assemblies in solution and play a major role in a variety of waterborne technologies including paints, inks, drill fluids, pharmaceutical, paper-making and cosmetics. [7-13]

Copolymer based on polyacrylamide is one of the most important hydrophobically modified polymers which has been intensively investigated due to its low price, bio-compatibility and widespread applications.[14] Some difficulties in preparing hydrophobically associative polyacrylamide (HAPAM) arise from the insolubility of the hydrophobic monomers in water. To overcome this problem, several methods have been developed. The two major of them are: (1) Polymerization in a polar organic solvent or organic solvent/water mixture, in which both hydrophilic and hydrophobic monomers are soluble. Generally, the resulted copolymers are not soluble in such a reaction medium and precipitate out. In conventional solution polymerization, different monomers randomly distribute within the reaction medium and products.[15, 16] However, in a number of developed systems of solvent or solvent/water mixture, chain transfer reaction exerted negative effects on copolymerization and molecular weight.[17] (2). Micellar polymerization is the most widely used method for the synthesis of HAPAM, in which hydrophobic monomers are solubilized in a synthetic system by surfactants, generally sodium dodecyl sulphate (SDS).[6, 18-20] It was found the obtained copolymers have an essentially block-like structure, the hydrophobe-rich regions distributed along polyacrylamide backbone. However, sometimes the surfactants served in conventional emulsion/suspension polymerization system have some drawbacks, such as poor stability of the latex since the emulsifier attaches on the latex particle only in a physical manner, and some negative effects of the residual surfactants for the properties of the final products.[21-23] Polymerizable surfactants, or surfmers, had been developed to stabilize the emulsion/suspension system of synthesizing HAPAM.[24, 25] Surfmers could be not only copolymerized into polymer chain, but also strongly attached on to the latex particles with covalent linkage, resulting in better stability of latex than normal surfactant.[23, 26] Yujun Feng et al. reported HAPAMs prepared by post-modification, which was claimed a more effective way to control the composition of HAPAMs compared against micellar process.[27, 28] In summary, the compatibility of hydrophilic and lipophilic comonomers in system is the key point in preparing hydrophobically modified polyacrylamides. In practical terms, to seek out proper solvents is crucial for solution (homogeneous) copolymerization and for micellar (heterogeneous) copolymerization, the importance is to find out an effective surfactant.

In this study, preparation of HAPAM had been conducted in a water-free suspension system, above the melting point of monomers in non-polar solvents. A number of surfactants had been studied in stabilizing this water-free system. The relationship between the consumption of surfactants and the loading of monomers in such a system had been investigated as well. Crosslinked polyacrylamide microgel had been prepared successfully through this method also after introducing crosslinker in reaction. Furthermore, polymerizable surfactant had been employed not only as co-polymer in polyacrylamide molecular chain, but also as an emulsifier with a covalent bonding to the latex in system. In a water-free medium, hydrophilic monomers or co-monomers per-se can work as the medium to solubilize hydrophobic monomers, increasing the compatibility. Therefore, the feed ratio of the hydrophobe will not be limited as it is in a traditional aqueous polymerization system. Additionally, Products are dry powder and ready to use, compared to traditional synthesis that require post-treatments, such as energy intensive drying process. Furthermore, dry powders are stable and easier to store and transport than wet polymer solution.

2. Experimental

2.1. Materials

Synthesis works were carried out with commercially available monomers, initiators, and reagents. Octadecylamine (C18AM, 97%, Sigma Aldrich), acryloyl chloride (≥97%, contains ~400 ppm phenothiazine as stabilizer, Sigma Aldrich), trimethylamine (TEA, ≥97%, Sigma Aldrich), n-alkylacrylamide, methylene chloride (ACS reagent, ≥99.5%, contains 50 ppm amylene as stabilizer, Sigma Aldrich), hydrochloride acid (concentrate, certified, Fisher Chemical), were used to prepare n-alkylacrylamide. Acrylamide (AM, ≥98.0%, Alfa Aesar) was used to copolymerize with octadecylacrylamide to synthesis HAPAM. 2, 2′-Azobis (2-methylpropionitrile) (AIBN, 98%, Sigma Aldrich) worked as initiator. Solvents used in polymerization included mineral oil (pure, Acros Organics), toluene (AR, ACS, Fisher Chemical), xylenes (Mixture of ortho-, meta-, and para- isomers and may contain some ethylbenzene, certified ACS, Fisher Chemical). Acetone (certified ACS, Fisher Chemical) was employed to wash products. Potassium bromide (KBr, ACS reagent, ≥99.0%, Fisher Chemical) was used for Fourier Transform Infrared Spectroscopy. Deuterium oxide (D_2O, 99.9 atom % D, ISOTEC), Dimethyl sulfoxide-d_6 (DMSO-d_6, 99.9 atom % D, Sigma Aldrich) were solvents in NMR test. A 100 ml three neck flask was used in reaction, inner surface of which was modified by octadecyldimethylmethoxysilane (ODMS) (97% purity, Petrarch). Homogenizer (7x195 flat generator with rotor PG7, 6XM 3xL12, IKA) was employed to do emulsifying.

2.2. Synthesis Work

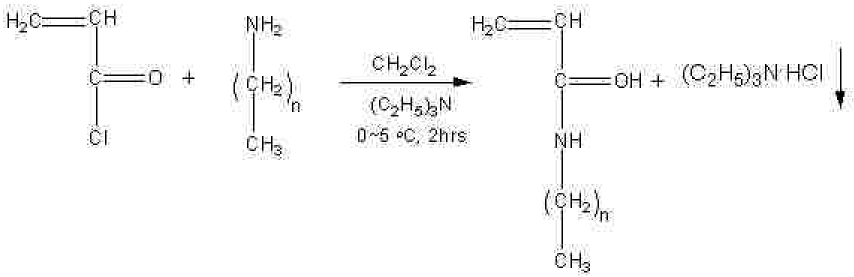

Fig. 1. Synthesis of N-alkylacrylamide.

2.2.1. N-alkylacrylamide

Octadecylacrylamide were prepared reaction of acryloyl chloride with the corresponding N-alkylamine, according to the classical procedure[29, 30]. (See Figure 1) A 250 ml, condenser, and an addition funnel. After purging with argon, the octadecylamine (0.11 mol) was dissolved in 100 ml of methylene chloride (CH_2Cl_2) and placed in the flask. The solution was then cooled to 0 ℃. Acryloyl chloride (0.11 mol) was dissolved in 100 ml CH_2Cl_2 and then slowly added to the reaction flask over a period of 2.5 h at such a rate that the temperature did not exceed 5 ℃. The resulting mixture was stirred below 5 ℃ for 2h. Then triethylamine hydrochloride was removed by filtration, and the obtained product-solvent mixture was washed by 0.1% HCl for three times. Rotary evaporator was employed to remove CH_2Cl_2, and the crude product, alkylacrylamide was collected with recovery of 77.1%

2.2.2. Heterogeneous polymerization (inverse suspension polymerization)

The inner surfaces of 100 ml and 250 ml four-neck reaction flask employed in this polymerization were modified from polar to non-polar by refluxing with ODMS-toluene solution. The flask was equipped with a magnetic stir bar, a condenser, a thermometer, and heating mantle. ODMS-toluene solution in flask was heated up at 120 ℃ for overnight and then the mixing solution was discarded. Afterwards, the reaction flask was rinsed using DI water for three times and dried at 120 ℃ in an oven.

Copolymers of AM and octadecylacrylamide were prepared by a solvent-in-oil(S/O) water-free suspension polymerization in a flask after inner surface modification. The four neck flask was equipped with water bath, a homogenizer, a condenser, a thermometer, an argon inlet and a bubbler. Firstly, mineral oil as non-polar solvent and octadecylacrylamide (0.5, 1, 2, 4 mol-%, based on AM), and designed amount of acrylamide were added into the flask. Oxygen was purged out from the system with argon flow for 30 minutes. The system was heated up just above the melting point of monomers (85 ℃). Then the contents were emulsified with assistance of a high shear (12000 rpm) shearing by homogenizer. After shearing for 0.5~1 hour, AIBN/toluene solution (0.5 wt.-% AIBN / 2ml xylenes) was added into system in small portions at 10 minute intervals over 2 hours to initiate the polymerization. After heating and homogenizing for 3 more hours, 0.5 wt.-% AIBN within xylenes was added into system in one dose, and the reaction kept for another 1 hour. Then the reaction was stopped by removing heat and shear. The resulting dispersion was reduced in viscosity by adding xylenes and filtered to obtain powder. The obtained powder was washed with acetone for three times to remove un-polymerized monomers. Purified, dry copolymer microsphere was achieved by drying in a 1 torr vacuum oven overnight at 50 ℃.

2.3. Methods and Instrumentation

2.3.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the powder samples were recorded on a Nexus 470 FT-IR (Thermo Electron Corp.). Dry powder products were diluted by mixing dry polyacrylamide microspheres with KBr at a 1:100 (w/w) ratio. Spectra were collected at 2 cm^{-1} resolution in mid-IR region (4000–400 cm^{-1}).

2.3.2. Scanning electron microscopy (SEM) study

SEM was performed using a Hitachi S-4700 field emission microscope. Powder of polymer/copolymer microspheres was used directly. SEM samples were mounted to a stainless steel stub using conductive tape and sputter coated with Au/Pd. Images were obtained with ESI software.

2.3.3. Thermogravimetric (TG) analysis

Thermogravimetric analysis of crosslinked polymer/copolymer was performed on TA Instruments (TGA Q50, U.S.A). About 10 mg dry products were characterized by TG measurements under a nitrogen atmosphere. The samples were heated from 25 ℃ to 105 ℃ at a heating rate of 20 ℃ min^{-1}, and held isothermally at 105 ℃ for 30 min to volatilize the free water from the samples. The samples were then scanned from 105 to 800 ℃ to record mass loss at a heating rate of 10 ℃ min^{-1}.

2.3.4. Nuclear magnetic resonance spectroscopy (NMR)

The sample of poly (acrylamide-co-octadecylacrylamide) was investigated by liquid ^{1}H NMR (400Hz) 60 ℃, and solid ^{13}C NMR (400 Hz) at 25 ℃ by Bruker high-field 400 MHz spectrometer. Sample for liquid ^{1}H NMR was prepared by dissolving dry product powder in D_2O at 50 ℃ and kept stirring for one week. Crude dry product was used for solid ^{13}C NMR.

2.3.5. Apparent viscosity

Dry sample was weighed accurately, dissolved in warm distilled water (50 ℃) with stirring for at least one week, and then sat overnight. Afterward, the solution was diluted to prepare copolymer aqueous solutions with different concentrations. The apparent viscosities of various copolymer solutions were determined at a constant temperature of 30 ±0.5 ℃ with a Brookfield viscometer at a shear rate of 6 S^{-1}.

3. Results and discussion

3.1. Synthesis and Mechanism

Polyacrylamides were synthesized following the steps described in experimental part. Over twenty non-ionic surfactants had been studied in stabilizing our S/O suspension. Furthermore the surfmer was employed to stable the S/O suspension, and also participated into the polymerization to make HAPAM.

3.1.1. Effect of reaction flask polarity

In this reaction, the neat inner surface of the glass reaction flask could introduce polymer particle aggregation and adhesion on the reactor wall. Wall adsorption was controlled when inner surface of the reaction flask was modified by a long aliphatic chain coating.

3.1.2. Effect of surfactants on stability of system

The suspension polymerization of acrylamide was studied in a water-free system. AM was dispersed in non-polar solvent, mineral oil, in a molten liquid state. With the assistance of proper surfactants and high shearing, the small droplets of the AM liquid were dispersed in a comparable stable state and formed a kind of solvent in solvent suspension. A number of surfactants were studied to stabilize the water-free S/O system, to minimize the consumption of surfactant and to maximize the feed of monomer amount. Over twenty non-ionic surfactants with different hydrophilic-lipophilic balance (HLB) had been investigated in stabilizing this water-free suspension system. Surfactants which can give stable milky suspension and particle products after polymerization were considered effective ones for this S/S suspension system, see Table 1, marked as stable (S). For unstable suspension systems, the added surfactants could not emulsify the system effectively to give phase-separated layers even after high speed shearing, marked as unstable (U). Generally, surfactants with low HLB values (<7) stabilize water-in-oil (W/O) suspension s/micellar (W/O surfactants), while surfactants with high HLB values (>7) stabilise oil-in-water (O/W) suspension /micellar (O/W surfactants).[33, 34] From the experiment results, surfactants with low HLB worked better than the surfactants with high HLB for this S/O suspension system. The reason is surfactants with low HLB have a structure of small polar (hydrophilic) head and long non-polar (hydrophobic) tail, which enables their small head go into polar liquid monomer droplets while their long tail extend in outside non-polar hydrophobic medium to stabilize the polar droplets in our S/O system.

Table 1
List of surfactants and their performance used in the water-free S/O suspension polymerization system.

Surfactant	Comments	Result Stable/Unstable
Oleic Acid	HLB = 1	S
SorbitanTrioleate (Span 85)	HLB = 1.8	S
SorbitanTristearate (Span 65)	HLB = 2.1	S
SorbitanMonostearate (Span 80)	HLB = 4.7	S
Tergitol 15-S-3	C12-C14 Secondary alcholethoxylate with 3 moles of ethylene oxide (EO); HLB = 8.3	U
Igepal CO-520	HLB = 10	U
Igepal CO-530	HLB = 10.8	U
Neodol 1-3	HLB = 8.7	U
Neodol 1-5	HLB = 11.2	U
Neodol 1-7	HLB = 12.7	U
Polysorbate 60 (Tween 60)	HLB = 14.9	U
Polysorbate 80 (Tween 80)	HLB = 15	U
Ethomeen C/15	HLB = 15	U
Ethomeen C/25	Bis(2-hydroxyethyl) cocaalkylamides	U
Butoxyethanol	-	U
Surfynol CT-141	-	U
Calamide CW-100	Modified with coconut diethanolamide	U
Calamide CWT	Modified with coconut amidesoapsueramide	U
Calamide F	Vegetable oil, diethanolamide	U
Ethomeen S/12	Bis(2-hydroyethyl) soyaalkylamines	U
Calimulse PR	Isopropylamine branched akylBenazene	U

S:stable; U: unstable

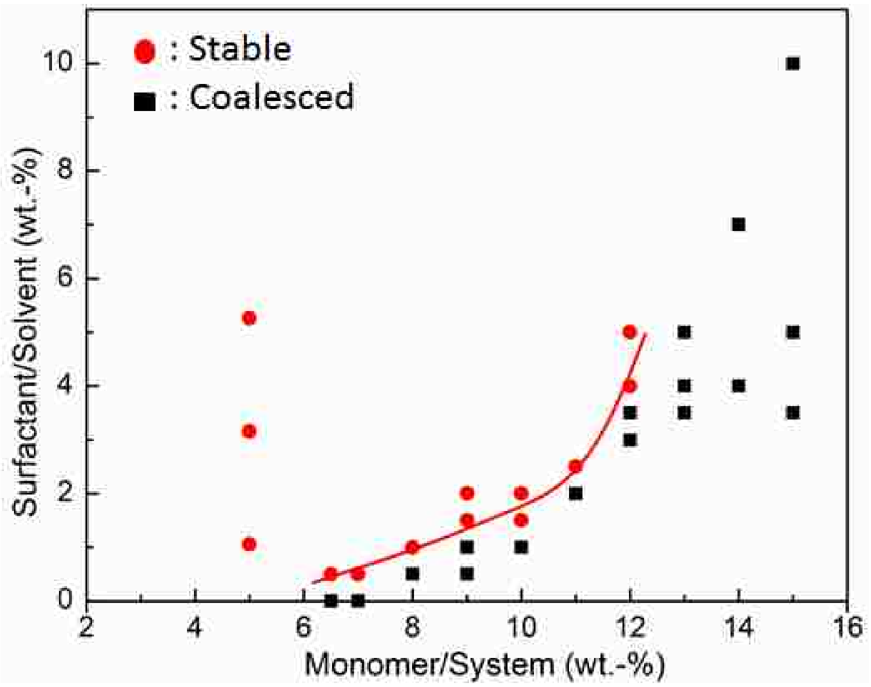

Fig. 2. Phase diagram: stable suspension of surfactant and monomer.

Surfactant Span-85 was selected to study the effect of the surfactant's amount on stabilizing the S/O suspension system to minimize the consumption of the surfactant and maximize the addition of monomer. The relationship between the feed of acrylamide and the amount of surfactant was displayed in Figure 2. In a low monomer feed, only a little bit surfactant is required to stabilize the suspension. The minimum required amount of surfactant is in a direct proportion to the feed of monomer. When the feed of monomer is more than 12 wt. -%, it is hard to stabilize the S/O suspension even consuming over 5 wt.-% surfactant. A heavy heat release had been observed during the polymerization, especially with high monomer feeding. In normal W/O system, monomer was dissolved in water to form aqueous phase generally with ratio less than 60 wt.-%.[35-37] In our S/O system, polar in non-polar suspension system, pure liquid monomer formed the polar phase dispersed in non-polar phase. The monomer ratio reached to 100 wt.-%, without water content.

3.1.3. Copolymerization of AM and octadecylacrylamide

Different from the normal suspension/micellar polymerization, in which the surfactant only helps to emulsify the system and will be discarded after polymerization, the sufmer can work not only as emulsifier but also can be polymerized into polymer chain. N-alkylacrylamides are common vinyl hydrophobic monomers to be introduced into polyacrylamide to make HMPAM by micellar polymerization. Generally, extra surfactants are required to solubilize n-alkylacrylamides.[3, 29, 38, 39] In our system, n-alkylacrylamide per se worked as surfactant to form stable the system, see Figure 3.

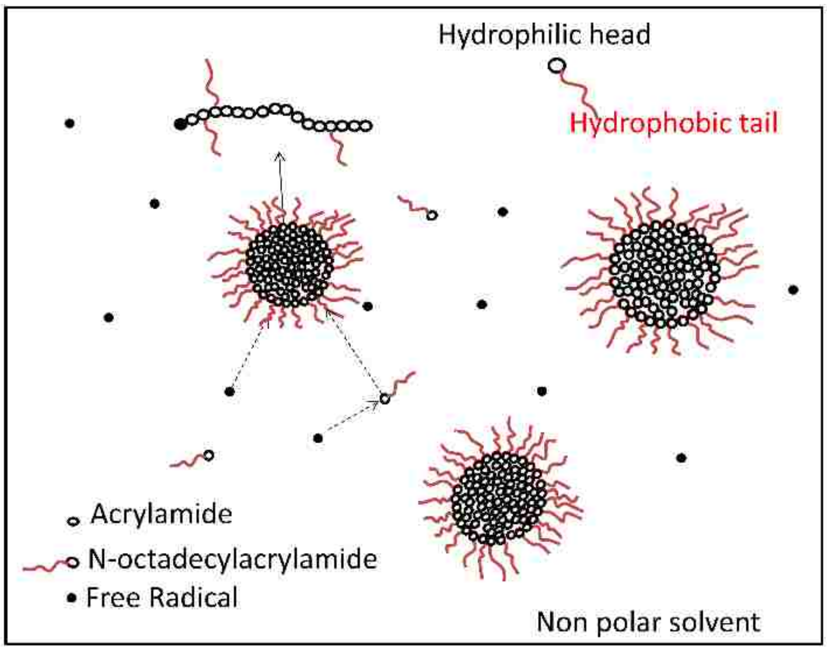

Fig. 3. Schematic representation of the copolymerization mechanism in the water-free S/O system: hollow black circle, water-soluble monomer, AM; red circles with an attached line; solid black circle: free radical.

Micellar polymerization is the most common method in synthesizing HAPAM. The ‘microblocky’ segmental structure has been postulated for a number of years.[40-43] In micellar polymerization, the hydrophobic monomer is solubilized within surfactant micellar, whereas acrylamide monomer is dissolved within continuous aqueous medium. At beginning, AM is initiated by water soluble initiator and started polymerization. Polymer chains propagate mainly in aqueous phase. When a growing radical moves into micellar, the solubilized hydrophobic monomers are polymerized immediately. This polymerization is conducted in a local hydrophobe rich micelle, resulting in a hydrophobic blocky structure in the copolymer chain[44]. However, it is unclear about the micro structure of the poly-(acrylamide-*co*-alylacrylamide) prepared by water-free suspension system. Supposedly the molten acrylamide monomer liquid was dispersed within a non-polar solvent to form a suspension with the assistance of surfactant. Then the oil soluble initiator creates the free radical in continuous oil phase. When the free radical moves into the micelle, chain propagates immediately and both the acrylamide

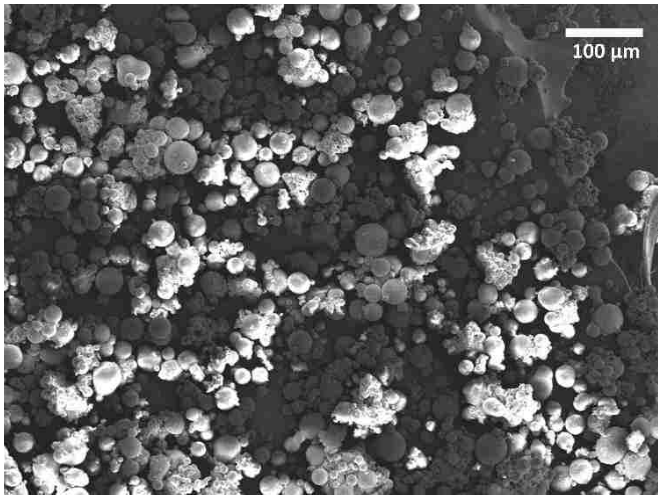

Fig. 4. The SEM picture of crude poly-(acrylamide-co-octadecylacrylamide).

monomer as well as the hydrophobic monomers within micelle will be polymerized into polymer chain. Figure 4 shows the SEM picture of the crude product. The spherical particles were achieved after polymerization conformed to our proposed mechanism.

Water-free S/O suspension polymerizations of acrylamide and poly (acrylamide-co-octadecylacrylamide)s were carried out isothermally over the temperature of 85 ℃. For the synthesis of polyacrylamide, surfactant Span 85 was used as surfactant, with 1.5 wt-% of mineral oil. For the hydrophobically modified copolymer, octadecylacrylamide was used as surfactant and hydrophobic monomer with designed amount. The specific experimental conditions for each polymerization are listed in Table 2.

Table 2
Experiment conditions for the Hydrophobic Modified of Poly-(acrylamide-*co*-octadecylacrylamide).

Sample	**AM (mol.-%)**	**C18AM (mol.-%)**	**Conversion**	**Solubility**
PAM	100	0	71.2%	Easily Soluble
C18 (0.5%)	99.5	0.5	81.6%	Semi cloudy solution
C18 (1%)	99	1	83.7%	Cloudy solution
C18 (2%)	98	2	86.7%	Cloudy solution
C18 (4%)	96	4	86.5%	Difficult to dissolve

Total monomer concentration = 5 wt.-%; [AIBN] = 0.1wt.-% of monomer; T=85 ℃.

The solubility of the products are not good as the products made by polymerization with water as solvent for monomers. The reason could be: (1).

hydrophobic out layer of the particle; (2). Water-free system made amide group hard to hydrolyze.

3.2. Structure and Thermogravimetric Analysis

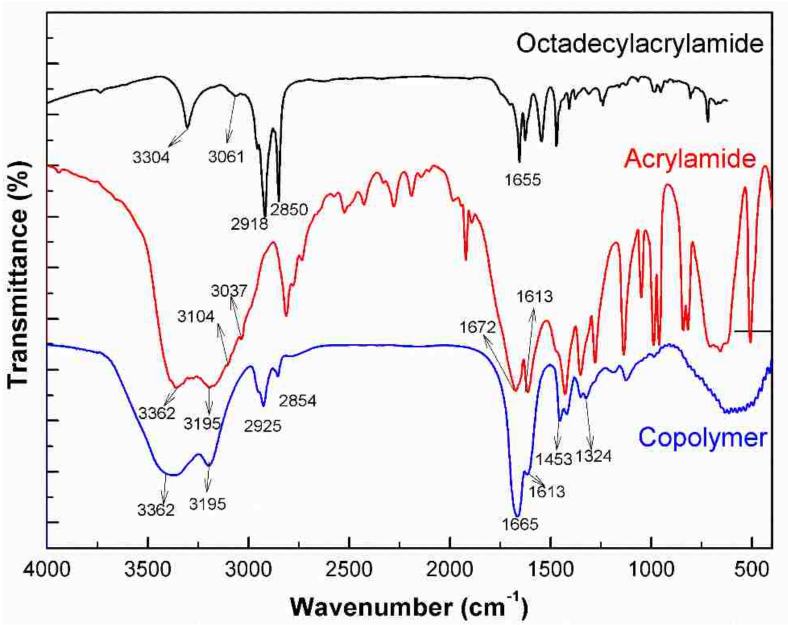

Fig. 5. Foruirer transfer infrad (FTIR) spectra of octadecylacrylamide, acrylamide and poly-(acrylamide-*co*- octadecylacrylamide).

The structures of monomers, octadecylacrylamide, acrylamide and co-polymers of them were confirmed by FTIR spectroscopy, see Figure 5. In the spectra of octadecylacrylamide, the bands at 3304 cm^{-1}, 1545 cm^{-1} and 1254 cm^{-1} were attributed to the N-H; The absorption at 1655 is due to the stretch vibration of C=O. For acrylamide, the absorptions at: 3336 cm^{-1}, 3195 cm^{-1} absorptions reflect vibrations of N-H;

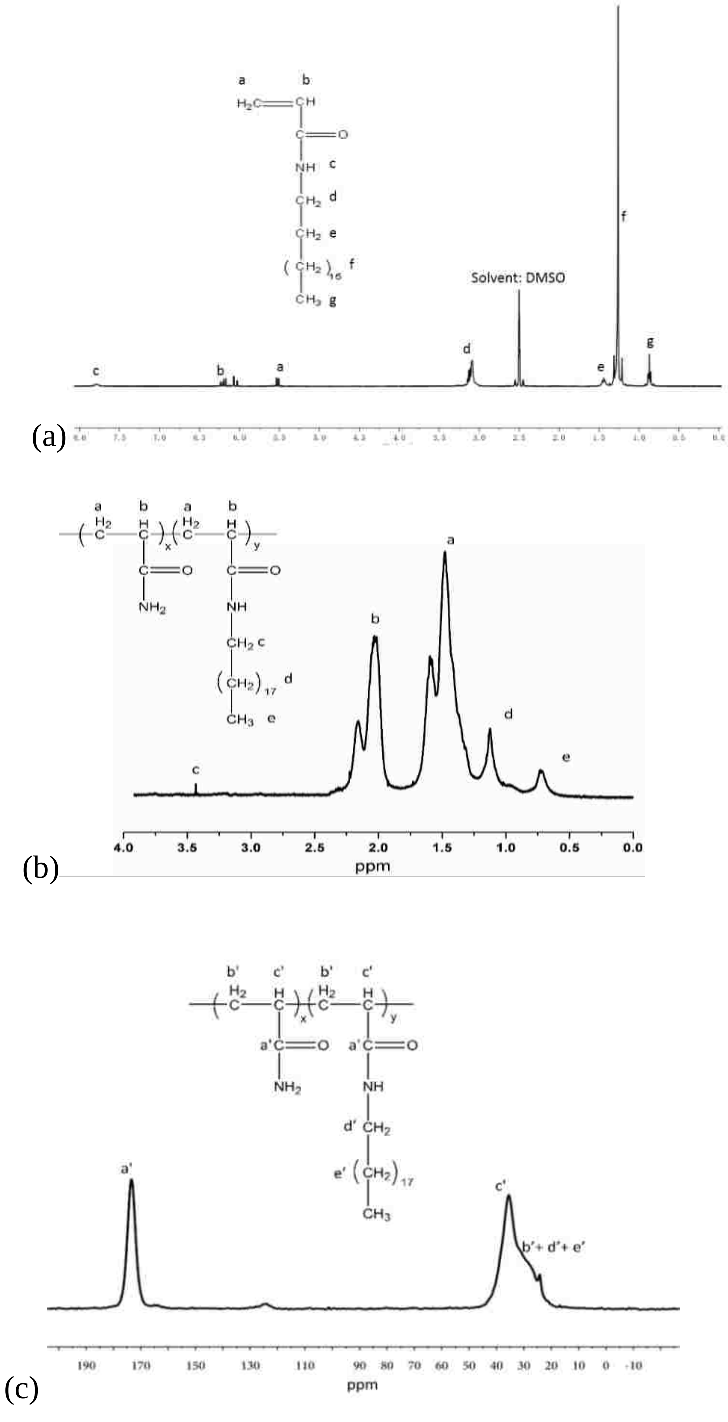

Fig. 6. (a) ^{1}H NMR of ocadecylacrylamide (b) ^{1}H NMR and (c) ^{13}C NMR spectra of poly-(acrylamide-*co*-octadecylacrylamide). For liquid 1H NMR, poly-(acrylamide-co-octadecylacrylamide) with 2 mol.-% octadecylacrylamide. For solid 13C NMR, poly-(acrylamide-co-octadecylacrylamide) with 4 mol.-% octadecylacrylamide.

Absorptions of C=C and C=O stretching vibration show up at 3037 cm^{-1} and 1672 cm^{-1} respectively. In the spectra of copolymer: the bands around 2925 cm^{-1}, 2854 cm^{-1}; 1453 cm^{-1} are owing to stretch vibrations of C-H; the characteristic peaks at 1665 cm^{-1} and 1324 cm^{-1} are vibrations of C=O and C-N.

Synthesized ocadecylacrylamide and the copolymer structure was determined by ^{1}H NMR and ^{13}C NMR, see Figure 6. Due to high viscosity and poor solubility, liguid ^{1}H NMR was conducted at 60 °C for hydorphobically modified polyacrylamide with 2 mol.-% aklyacrylamide. Solid ^{13}C NMR was taken of polyacrylamide with 4 mol.-% aklyacrylamide. The assignments of each peak are in agreement with the literature data.[45, 46]

3.3. Effect of Hydrophobe Content

Thermal properties of the poly (acrylamide-co-octadecylacrylamide) were characterized by TGA. According to Figure 7, crude dry product were obtained by removing free water and solvent isothermally at 105 ºC. Bulk water and solvents were about 5~9 -% mass of samples with 0~2 mol-% hydrophobe. From 110 ºC to 220 ºC, the weight loss during this period is caused by the loss of bonding water and solvent during the polymerization and purification supposedly. Obviously, copolymer with more hydrophobe had more weight loss during this period. Because the incorporated hydrophobe can break the compact packing of pure PAM, which can created more free space to absorb polar water and solvent during the purification or from the environment. Furthermore, the bonded water and solvent which is more close to the hydrophobe would be lost at lower temperature, resulting in some flocculation on the curves (red dash circled area in Fig. 7.).

There are two main thermal degradations of the copolymer, typical of polyacrylamide. The first degradation temperature (T_d) is onset at 270 ºC. The degradation evolves ammonia from thermal imidization of polyacrylamide or absorbed mineral oil in microspheres.[47, 48] The main weight loss onset at 380 ºC, which is resulted from the degradation of polymer backbone.

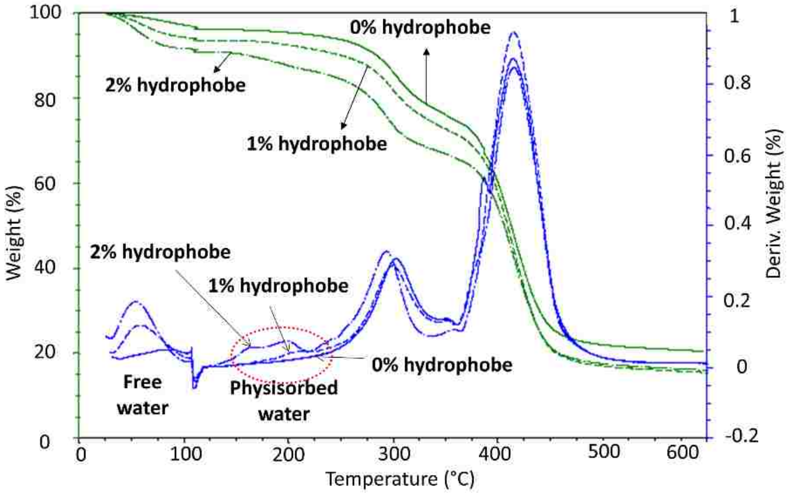

Fig. 7. Thermogravimetric (TG) curves of the hydrophobically modified copolymer.

Figure 8 displays the relation curves of the apparent viscosity of the HMPAM with different hydrophobe. For HPAM, the viscosity was increased steadily, while, at concentration around 1500 mg/L, an abrupt change occurred on HMPAM. This is the critical association concentration (*C**) at which not only intermolecular association but also intramolecular association happening. At the same concentration, higher viscosity was observed for the copolymer with more hydrophobe, indicating association is strengthened by increasing the hydrophobically dynamic crosslinking points created by the hydrophobes along HMPAM chain.

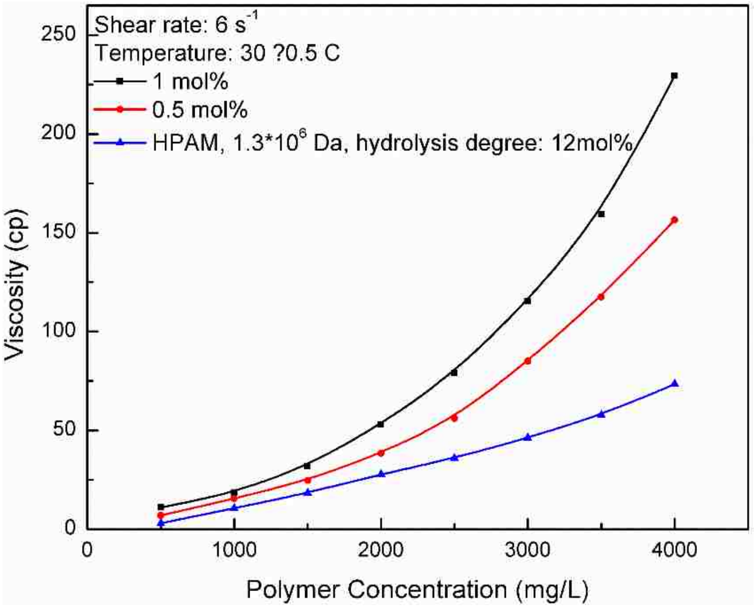

Fig. 8. Apparent viscosity of aqueous solution as a function of copolymer concentration. Temperature: 30±0.5 ℃, shear rate: 6 S^{-1}.

4. Conclusions

Polyacrylamide and poly (acrylamide-co-alkylacrylamide) had been syntheized by a water-free solvent in oil suspension polymerization. Alkylacrylamides were used as sufmer which can stabilize the suspension system as a surfactant and also polymerized into copolymer to introduce hydrophobic domain. Compared to hydrophobically modified polyacrylamides prepared by traditional methods, higher mol.-% hydrophobe could be incorporated into copolymer and more than this number could be achieved by virtue of this water-free suspension polymerization with alkylacrylamides as polymerizable surfactants. Indeed, the solubility of the obtained products are not good as other hydrophobic modified polyacrylamide prepared by other polymerization with water as the solvent for monomers. This method has potential to be used in preparing swell-delayed polyacrylamides or microgels which could be used in oil recovery.

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III. Temperature-sensitive polyacrylamide microgels and pore modeled oil recovery performance

Zun Chen,[1] Thomas P. Schuman,[1]Jiaming Geng,[2] and Baojun Bai[2]

[1] Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65401

[2] Department of Petroleum Engineering, Missouri University of Science and Technology, Rolla, MO 65401

Correspondence to: Thomas P. Schuman (E-mail: tschuman@mst.edu)

ABSTRACT

Polymer gel treatments can be a cost-effective method to improve sweep efficiency and reduce water production during oil recovery operations. In this paper, a novel suspension polymerization method was developed to synthesize a temperature-sensitive microgel. Compared to conventional methods, the microgel was prepared above the melting point of the monomer in a non-polar solvent without water. Dry microspheres were obtained which can be readily used without post-treatment. Two different crosslinkers were employed in the suspension polymerization synthesis to give the particles thermally responsive aqueous swelling properties. After entering target pore channels, gel particles can expand to desired sizes to realize flow profile changes within in a reservoir formation. When dispersed into water under lower temperatures (ambient to 40 °C), the original dry particles can swell about 18 times their original size. Exposure to a harsher environment (e.g., 80 ℃) resulted in cleavage of the labile crosslinking agent and some chain cleavage with further size expansion. A Millipore film filtration model system was adopted to evaluate pore occlusion performance of the gel particles. It was found that the nuclear pores were effectively sealed by swollen microgels when gel particle size were similar to or smaller than the membrane pores and pore separation. Gel particles which are much larger than the pore size did not produce effective occlusion of filtrate flow due to steric hindrance.

KEYWORDS: crosslinking; microgels; stimuli-sensitive polymers; solvent in solvent suspension polymerization; polyacrylamide

INTRODUCTION

Crude oil is an internationally important commodity resource for energy and chemical industries. After primary and secondary flooding of the formation, more than two thirds of the resource still remain in the reservoir[1]. In these tertiary reservoirs, direct water or polymer-assisted flooding recovery become inefficient for displacing oil due to pore size heterogeneity of the geologic formations. The flooding agent, e.g., water, prefers paths of lowest flow resistance. Wider pore channels provide less shear resistance compared to narrow pores of higher resistance flow. Preferential flow in previously swept, larger pores bypasses low permeability zone leading to excess water production, i.e., mostly flooding fluid and less of the desired oil product.

Polymer gels can be cost-effective methods to improve sweep efficiency and reduce excess water production for an enhanced oil recovery (EOR).[2,3] Polymer gel treatments of injection wells are being developed to preferentially limit flooding flow through larger pore conduit zones. When gels carried by flooding fluid are injected into reservoir, the gel particles are prone to enter channels or fractures with lowest resistance pressure. Gels may then expand, aggregate or occlude the region to affect the flow resistance. If conduit channels are occluded, flooding flow is shifted to new, oil bearing areas in the reservoir so more of the remaining oil can be extracted.

Two types of gels are currently applied in controlling conformance,[4] in-situ crosslinking gels[5-7] and preformed particle gels (PPGs).[8-19] For in-situ crosslinking gels, a mixture of polymers and crosslinking reagents are injected into a target formation to polymerize at reservoir temperature to form the ‘in-situ gel’ that is intended to fully or partially seal a formation region.[9,10,14] PPGs, on the other hand, are prepared before injection. PPGs are crosslinked, dry particulate hydrogels, that can expand tens or hundreds times of their original size when dispersed in water.[10] Polyacrylamides are the main polymers used for preparing PPGs due to acrylamide’s cost, facile polymerization, polyacrylamide aqueous solution properties, and gelling capability of the polymer.

Two main methodologies have been adopted in synthesis of polyacrylamide PPGs. The first method is solution polymerization[20], which requires all monomers, crosslinkers, and waterborne initiator are added to solvent, typically water to form a bulk gel. The obtained bulk gel is then dried and cut or ground into dry particle gels, which are dispersed in water as an injectable gel particle dispersion. Bai, et al.[8,9,12-17,21] have conducted synthesis, lab tests and pilot testing, as well as field applications of bulk PPGs.

A second method to synthesize PPGs is through inverse suspension polymerization,[22-24] with water, a hydrophobic non-polar solvent, surfactants, and initiator to form a water in oil (w/o) system to synthesize polyacrylamide microgels. Waterborne or oil soluble initiators could be used to initiate free radical polymerization through different mechanisms. Microgels prepared by this method have been studied in EOR application for several years.[25,26] For instance, Wang, et al.[27] reported a polyacrylamide EOR nanogel with an original diameter of approximate 50 nm that expanded to several micrometers upon swelling in pure water.

PPG microgels synthesized by traditional polymerization mentioned above need energy intensive post-treatment to isolate from water phase into dry particles. In this paper, a novel PPG synthesis method is developed based on an inverse suspension polymerization but in the absence of water. Dry product powder is obtained by polymerization above the melting point of the monomer. In this way, the products are dry solid microspheres, readily separated from solvent. Compared to traditional inverse suspension polymerization, the monomer in oil system employs less surfactant, the process is less energy intensive, and solvents can be recycled.

Two different kinds of crosslinkers were introduced to prepare the microgel. One reagent was considered to be thermally and hydrolytically stable. A second was considered thermally labile, which could be broken under the stimuli of raised temperature in an aqueous environment. The gel particles initially absorb water and swell upon dispersion in water. When the labile crosslinked particles in water were heated, the microgel further expanded under constraint of the remaining crosslinker.

Pore occlusion efficiency by dispersions of swollen PAM microgels was evaluated by a nuclear-pore film filtration model system. Traditional evaluation methods,[24,28,29] such as core-flooding test, can show the overall information of oil recovery efficiency. Whereas, the membrane filtration system is designed to investigate how microspheres plugged the nuclear-pores and their plugging properties[22,30]. In this paper, the matching behavior between the size of microgel particles and pores and the pitch of pores as well as the plugging performance of those microgel particles were studied.

EXPERIMENTAL

Materials

Preparation of polyacrylamide microgels was carried out with commercially available monomers, initiators, and reagents. The monomer used in this work was acrylamide (AM) (purum, ≥98.0%, Sigma Aldrich), with poly (ethylene glycol) diacrylate (PEGDA) (average M_n: 250, stabilized with 100 ppm monomethyl ether hydroquinone, Sigma Aldrich) and N,N′-methylene-bisacrylamide (MBAM) (~99%, Sigma Aldrich) as crosslinkers. Initiator used for polymerization was azobisisobutyronitrile (AIBN) (98%, Sigma Aldrich). Solvents used in polymerization included mineral oil (certified ACS, Fisher Chemical), xylenes (certified ACS, Fisher Chemical), acetone (Chromasolv Plus, for HPLC, ≥99.0%, Sigma Aldrich), toluene (certified ACS, Fisher Chemical), and deionized (DI) water (18.2 MΩ) produced by Milli-Q Plus system from Millipore (Billerica, MA). Surfactant to stabilize the oil in oil system was sorbitan trioleate (Span-85, viscosity 1200~2000 mPa-s, 20 ℃, Sigma Aldrich). A 250 mL three neck flask was used for gel polymerization; the inner surface of which was modified by octadecyldimethylmethoxysilane (ODMS) (97% purity, Petrarch). A homogenizer mixer (PowerGen 1000, FisherSci; 7x195 flat generator with rotor PG7, 6XM 3xL12, IKA) was employed to disperse the polymerization system.

Potassium bromide powder (KBr, ACS reagent, ≥99.0%) was used as window material for collecting Fourier transform infrared absorption spectra.

Preparation of Polyacrylamide Microgel via Water Free Inverse Suspension Polymerization

The inner surface of 250 mL four neck reaction flask employed in this polymerization was modified from polar to non-polar by refluxing with a 1% ODMS in toluene solution. The flask was equipped with a magnetic stir bar, a condenser, a thermometer, and heating mantle. The ODMS-toluene solution in flask was heated to about 110 ℃ overnight and then the contents were discarded. Afterwards, the reaction flask was rinsed using DI water three times and dried at 120 ℃ in a conventional oven.

Crosslinked polyacrylamide microgels were prepared by a water-free suspension polymerization in modified flask. The four neck flask was equipped with water bath, a homogenizer, a condenser, a thermometer, an argon inlet and a bubbler. Firstly, 90 g mineral oil and 1.8 g Span-85 were added into the flask. The Span-85 was dispersed in mineral oil to form a homogeneous mixture, to which 10 g AM monomer, 0.033 g PEGDA, and 0.0033 g MBAM were added.

Oxygen was purged from the system with argon flow for 45 minutes. The system was then heated to 85 ℃, the melting point of acrylamide. The contents were emulsified with assistance of the high shear (12000 rpm) homogenizer. After shearing for 0.5~1 hour, AIBN in xylene solution (0.01 g AIBN / 5 mL xylene) was added into system in small portions at 10 minute intervals over 2 hours to initiate the polymerization. After heating and homogenizing for 3 more hours, a 0.01 g AIBN within xylenes was added into system in one dose, and the reaction kept for 1 hour. The reaction was stopped by removing heat and shear. The resulting dispersion was reduced in viscosity by diluting with xylenes and filtering to obtain powder. The obtained powder was washed with acetone three times to remove un-polymerized monomer and surfactant. Purified, dry acrylamide microsphere gels were achieved by drying in a 1 torr vacuum oven overnight at 50 ℃.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of the powder samples were recorded on a Nexus 470 FT-IR (Thermo Electron Corp.). Sample was diluted by mixing dry polyacrylamide microspheres with KBr at a 1:100 (w/w) ratio. Spectra were collected at 2 cm^{-1}resolution in mid-IR region (4000–400 cm^{-1}).

Thermogravimetric Analysis (TGA)

TGA of crosslinked micro spheres was performed (Q50, TA Instrument, U.S.A). About 10 mg dry polyacrylamide microspheres were characterized by mass loss measurement under a nitrogen atmosphere. The samples were heated from 25 ℃ to 105 ℃ at a heating rate of 20 ℃-min^{-1}, and held isothermally at 105 ℃ for 30 min to volatilize the free water from the samples. The samples were then scanned from 105 to 800 ℃ to record mass loss at a heating rate of 10 ℃-min^{-1}.

Optical Microscope Study on the Microgel Swelling and Size

Swelling kinetics of microspheres was visualized using an Olympus IX-51 optical microscope (Olympus America, Center Valley, Pennsylvania). Samples were prepared by dispersing dry polyacrylamide particles into DI water at a concentration of 0.5 wt.-%. Dispersions were heated at 40 ℃ for two months and visualized. The fully swollen (40 ℃) microgel dispersions were then heated to 80 ℃ for one and half months till no obviously additional size change was observed. Within this period, an aliquot of the swollen microsphere samples was collected and placed onto a clean cover glass. The samples were imaged under the optical microscope and pictures taken. In order to improve particle surface contrast against the aqueous background, brilliant blue dye (Blue #1) was used to stain water swollen microgel surfaces. Particle sizes were analyzed and collected by the software Image-J. The swelling ratio (*S*) was calculated by the following equation:

$$S = V_s/V_d \qquad \text{Equation 1}$$

where V_s and V_d are respectively the measured volumes in the swollen and in the dried state, respectively.

Pore Occlusion Performance

The nuclear-pore membrane, model pore occlusion testing apparatus was originally described by Zhao et al.[22,31] The apparatus schematic is provided as Figure 1. Samples of swollen microgel dispersions were prepared by adding dry particles into DI water at a concentration of 0.5 wt.-%. Particle dispersion samples were placed into an oven at 80 °C, for two weeks to allow microgels to absorb water and swell to equilibrium size. The original dispersions were then diluted by DI water to different concentrations: 50, 100 and 250 ppm, respectively. Dispersions of these concentrations were injected to the injection membrane reservoir through the nuclear pore membrane sample holder. Volume of the filtrate as a function of filtration time was recorded during the injection process. The membranes employed spanned a series of pore sizes (0.45 µm, 0.8 µm, 1.2

μm, 5 μm, and 10 μm). A low differential pressure (10 psi) and a higher differential pressure (100 psi) were chosen for the pore occlusion simulation testing.

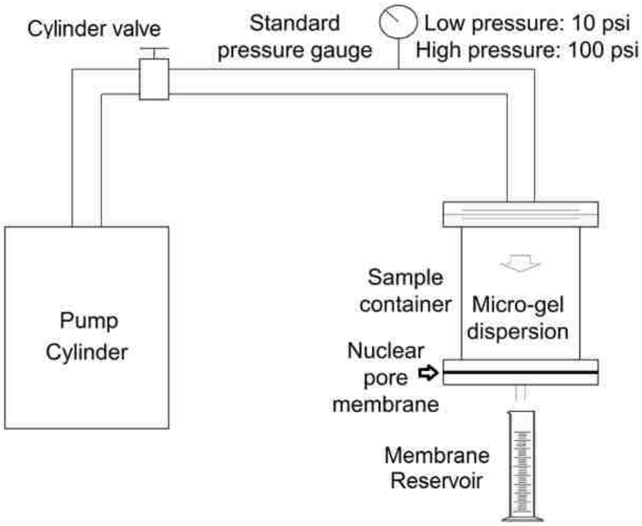

Figure 1. Schematic diagram of the pore occlusion filtration test apparatus.

Scanning Electron Microscopy (SEM) Study

SEM was performed using a Hitachi S-4700 field emission microscope. Powder of crosslinked polymer microspheres and blank membranes were used directly. SEM samples were mounted to a stainless steel stub using conductive tape and sputter coated with Au/Pd. Images were obtained with ESI software and analyzed by Image J (NIH) software to determine size distribution. Membranes were visualized for particle residues after the pore occlusion filtration test upon drying the membrane at ambient temperature. SEM imaging was conducted using a field emission source at a 5 kV accelerating voltage and 11 pA current at a working distance of 3~6 mm with an Everhart-Thornley detector.

RESULTS AND DISCUSSION

Inverse Suspension Polymerization without Water

A water-free, inverse suspension polymerization for synthesis polyacrylamide microgel was attempted. The detailed procedure is described in the experimental section. Crosslinked, dry polymer spheres were produced directly, with minimal need for post treatment of the products, e.g., dehydration, crushing or grinding. The reaction consumed little surfactant, ~2 wt.-% of the system, compared to normal inverse emulsion/suspension polymerizations with water, which can require more than a 10 wt.-% concentration in aqueous systems.[27,32-34] Solvents were recycled by distillation and reuse.

During initial polymerizations, it was observed that the polarity of the reaction (glass) flask inner surface affected the polymerization result. Product was observed to adhere and nucleate on the glass reactor wall when a clean glass inner surface was used. The adhering products were aggregated, dry, and firm polymer. As reaction continued, the aggregated particles would continue to grow on the aggregation with few free particles observed in the liquid suspension. However, the issue was preventable by treating the inner surface of the reaction flask with a long aliphatic chain (C-18) silane coating. Wall adsorption by polymer particles was then effectively prevented and normal suspension polymerization resulted.

Two crosslinking comonomers, MBAM and PEGDA, were employed in the reaction. Swelling expansions of the hydrogels were expected to have time-temperature dependency due to the combination of the dual crosslinkers with different thermal stability. MBAM was utilized as a thermally stable crosslinker, while the PEGDA was thermally labile.[15] MBAM was previously found to be stable to at least 90~100 ℃.[35,36] Owing to ether and ester linkages in the molecule, aqueous PEGDA was prone to degrade quickly when temperature reached 70~80 ℃.[15] A two stage expansion was desired, having a fixed, swollen particle diameter in aqueous dispersion at ambient temperature and then a second, larger diameter upon exposure to an elevated temperature.

Fourier Transform Infrared Spectroscopy

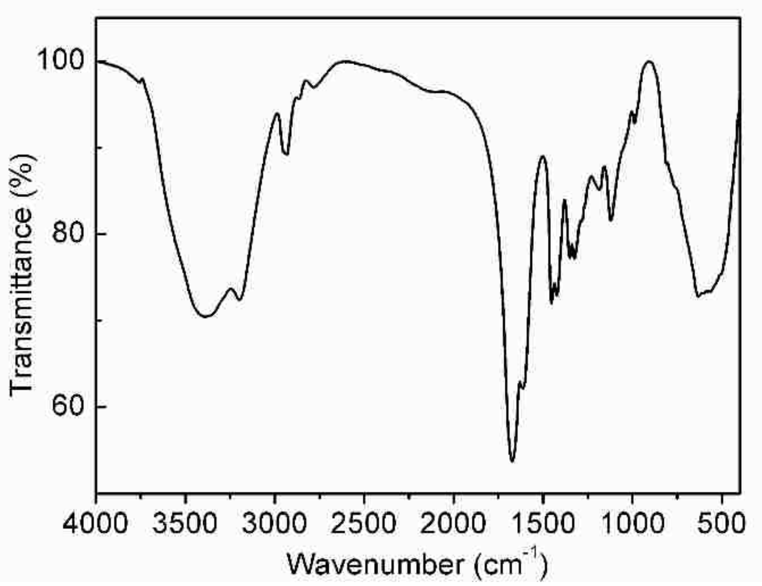

Figure 2. FTIR spectrum of polyacrylamide crosslinked microspheres**.**

The composition of the dry microspheres was characterized by FTIR spectroscopy (Figure 2) and was typical of polyacrylamide. The absorption bands at 3400 cm^{-1} and 3197 cm^{-1} are stretching vibrations of N-H. The characteristic absorptions at 1670 cm^{-1} and 1418 cm^{-1} are vibrations of the C=O (amide) and C-N, respectively, while absorptions at 2939 cm^{-1}, 2862 cm^{-1}, and 1450 cm^{-1} reflect vibrations of $-CH_2-$. Crosslink structures were not observable in the FTIR spectra since the concentration of crosslinkers was less than 0.5wt.-%.

Thermogravimetric Analysis

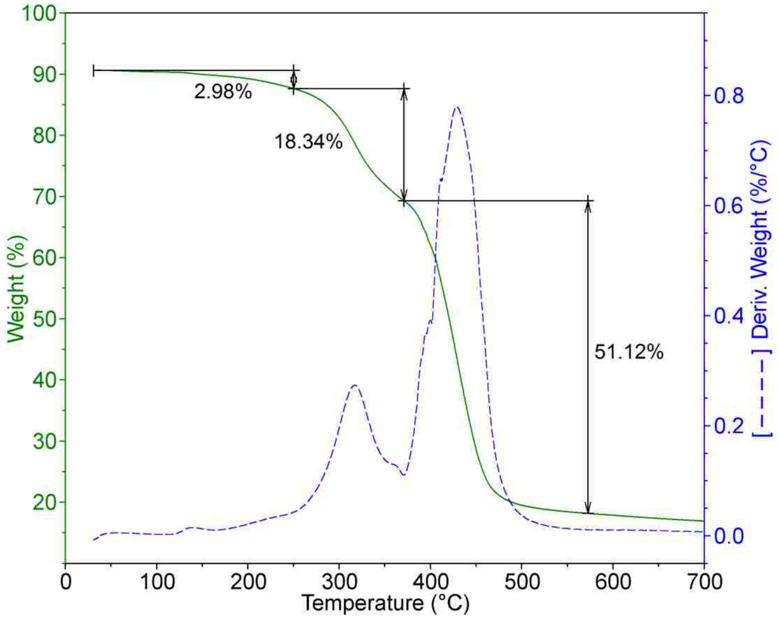

Figure 3. Thermogravimetric curve of the PAM micro-gel dry spheres, obtained after samples treated isothermally at 105 ℃ for 30 min.

Thermal properties of the microsphere solids were characterized by TGA. According to Figure 3, crude dry particles were obtained by removing free water and solvent isothermally at 105 ℃. Bulk water and solvent were about 9% of sample mass. A 3 % weight loss occurred below 250 ℃, due to absorbed and bonded water and solvent in the polyacrylamide. As the polar solvent used to wash the products, acetone (b.p. 56 ℃) would be expected to constitute the major part of volatile solvents since it could remain absorbed during synthesis but was not observed. Meanwhile, polymer can also absorb trace water from acetone and environment. The product had about a 97% non-volatile content.

There are two main thermal degradations of the microspheres, typical of polyacrylamide. The first degradation temperature (T_d) is onset at 270 ℃ with a weight loss of 18.3 %. The degradation evolves ammonia from thermal imidization of polyacrylamide[37-39] removing of unreacted monomer or absorbed solvent, mineral oil. The main weight loss of 51.1 % onset at 380 ℃ results from degradation of the polymer chain backbone.

Conformation and Size, Swelling Kinetics of Crosslinked PAM Microspheres

The dry solid polyacrylamide microspheres before swelling were imaged using SEM (Figure 4a). The average diameter of the dry microgel particles was 6.9 μm with standard deviation of 2.5 μm. Most particles are spherical, which was expected for a spherical drop of polar fluid in a non-polar solvent-solvent suspension. Non-uniformity of particle size indicated the polymerization was by suspension rather than emulsion process. High exothermicity caused by free radical polymerization may the other reason for such non-uniformity. During the synthesis process, molten acrylamide monomer drops were dispersed within non-polar solvent in the absence of water. Dry microspheres were obtained after polymerization.

The swelling kinetic of particle gels containing one crosslinker has been intensively studied.[40-43] and just one stage of expansion had been observed. In this paper, the produced microspheres showed different swelling kinetics as a function of temperature when dispersed into water. Two swelling stages, corresponding to the presence of the two different crosslinkers, were observed. Dry particles were firstly

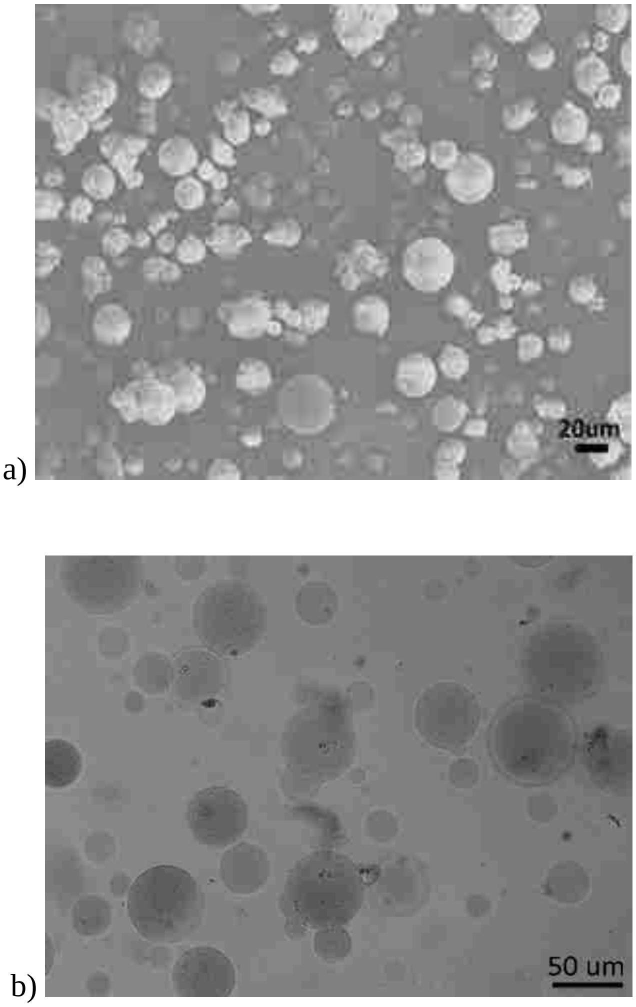

Figure 4. a). SEM of polyacrylamide dry particles; b). Microscopic image of swelled polyacrylamide microgels.

put into DI water under 40 ℃ for two months and swelling size was equilibrated. Polymer microgel particles swelled rapidly in first several days, after which the swelling speed slowed and became zero. After reaching equilibrium state at 40 ℃, the average volume of the swollen microgels divided by the volume of the dry microspheres (V_f / V_o) reached about 18 times the size of dry spheres.

When the temperature of the microgel dispersions were elevated to 80 ℃, the microgels experienced a second expansion stage after more than a month at the higher temperature. The particle sizes were measured by microscopic imaging of drop aliquots of microgel dispersion taken over time. At 80 ℃, the particles increased (= V_f / V_o) to 160 times the original size. Throughout the expansion process the polydisperse microgels retained a spherical conformation (Figure 4b).

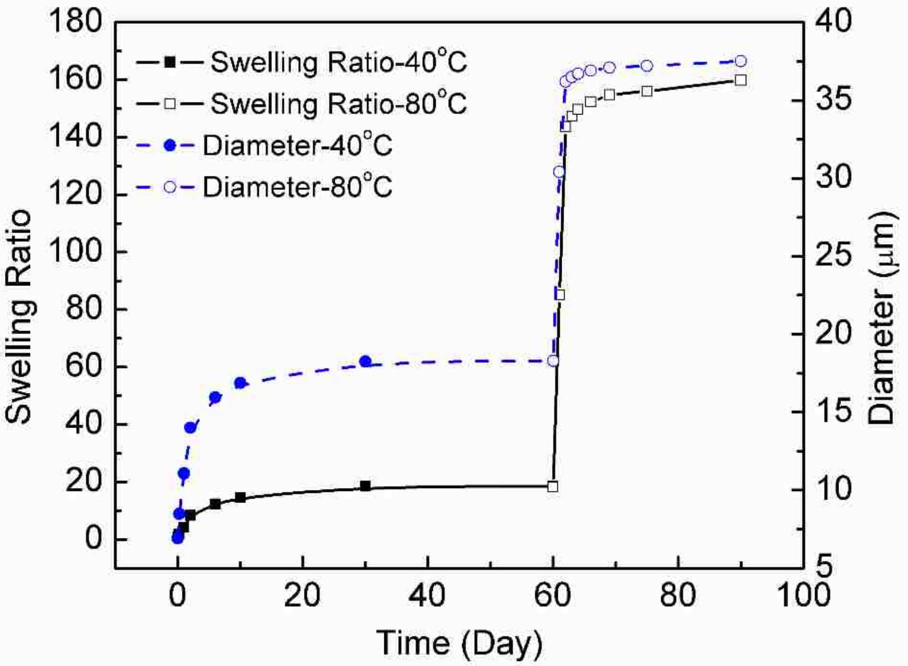

Figure 5. Swelling kinetic and diameter change of crosslinked microgels in DI water under 40 ℃ and 80 ℃. Different types of data are illustrated by different colors: black solid lines are swelling ratio and blue dash lines are diameter change. The filled symbols are data at 40 ℃ and unfilled symbols are data at 80 ℃.

Swelling kinetics are illustrated in Figure 5. Two expansion stages were observed by change in particle diameter and therefore volume. Under the lower temperature (40 ℃) swelling of microgel was constrained by both crosslinkers in a more compact structure. When the microgel particle dispersion entered the higher temperature stimuli, the labile crosslinker (PEGDA) was induced to cleave.[44] The secondary expansion corresponded to a loosened network upon breakage of PEGDA (Figure 6).

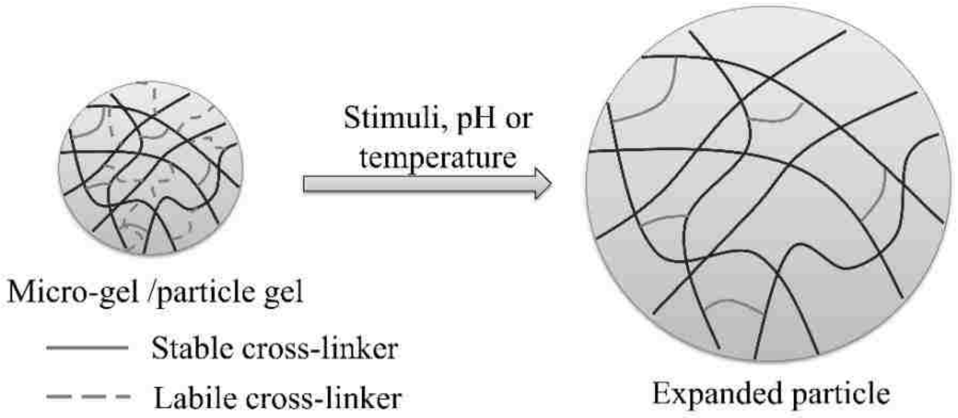

Figure 6. Proposed swelling mechanism of the crosslinked microgels in DI water at 40 ℃ and 80 ℃.

Crosslink density is one of the most important factors that determines the properties of crosslinked hydrogels and is typically reported as an average molecular weight (M_c) between crosslinks. The M_c of polyacrylamide hydrogels was calculated using the Flory-Rehner equation:[45,46,47]

$$M_c = \frac{\rho_p * V_1 (v_2^{\frac{1}{3}} - \frac{1}{2} v_2)}{-[ln(1-v_2)+v_2+\chi_1 {v_2}^2]} \qquad \text{Equation 2}$$

where χ_1 is the interaction parameter, V_1 is the molar volume of water (18.062 cm^3/mol), and ν_2 is the average volume fraction of polymer in the hydrogel when it reaches the equilibrium swelling state. The χ_1 parameter of crosslinked pure polyacrylamide hydrogel has been reported to be 0.48 at 25 ℃.[48,49]

The value of ν_2 can then be calculated using the following equation:[46,47]

$$v_2 = (\frac{1}{\rho_p})/[\left(\frac{S}{\rho_s}\right) + (\frac{1}{\rho_p})] \qquad \text{Equation 3}$$

In Equation 3, ρ_p is the polymer density (1.11 g/cm^3), S is the gel swelling ratio and ρ_s is the density of water. It is supposed that ρ_s =1 g/cm^3, yet It should be note that the water molecule in hydrogel are ordered which leading to a larger density than free water.

Table I. Measured Swelling Properties of Microgels Dispersed in DI water

Microgel Sample	**Swelling Ratio (S)**	**Mc (g/mol)**	**Mc* (g/mol)**	**Crosslinker efficiency**
Aqueous, 40 ℃	18	8.24 x 104	6.69 x 104	79.1%
Aqueous, 80 ℃	150	4.58 x 106	4.67 x 105	10.2%

The average molecular weight, M_c between crosslinks calculated according to the Flory-Rehner equation from swelling ratios and theoretical M_c* calculated through feeding amount are listed in Table 1. At low temperature, the swelling of microgel is controlled by two crosslinkers, MBAM and PEGDA. Through comparing M_c *and* M_c*, the efficiency of crosslinkers was 79.1% of theoretical. After high temperature stimuli, the swelling of the microgel was intended to be controlled by the quantity of thermally stable crosslinker (MBAM). However, the efficiency of the MBAM crosslinker was observed to be only 10.2%.

At high temperature, either only a portion of MBAM crosslinks were effective or additional swelling was observed due to polymer chain degradation[50,51] and/or hydrolysis of acrylamide groups to acrylic acid, changing χ_1. A six-carbon ring degradation structure was detected in polyacrylamide hydrogel exposed to the higher temperature by mass spectra, which indicated imidization with breaking of the polymer backbone. It should be noted that swelling expansion did not completely stop during the higher temperature observation. Hydrogels at 80 ℃ eventually dissolved as particle-solvent boundaries became blurred further supporting polymer chain degradation.

Pore Occlusion Performance

Nuclear-pore filtration membranes having consistent, cylindrical pores are a tool to simulate a single layer of porous medium for studying the pore occlusion behavior of the microgels.[22,31] A low, differential pressure of 10 psi was applied to push microgel-in-water dispersions through nuclear-pore membranes of varying pore size. Membranes of four pore sizes, 0.45 µm, 0.8 µm,1.2 µm, 5 µm, and 10 µm, were tested (Figure 7). The filtrate volume was recorded as a function of time to test the microgel dispersions' pore occlusion performance.

Pictures 7a and 7b, display a "spurt loss," which is the initial influx of fluid through a formation. Displacement and compression of the formation fluid[52] was then observed as a steady output of fluid volume. Flow resistance was observable to some extent but pores were not completely occluded by particles when membranes of pore sizes 0.45 µm or 1.2 µm, pores smaller than the average particle size, were tested. Lower concentration dispersions produced larger flow rate slopes of volume versus time. Gel particles inefficient in pore occlusion allowed more fluid volume to pass the membrane. After the spurt loss, only partial pore occlusion had occurred, which was indicated by an increasing total volume of filtrate.

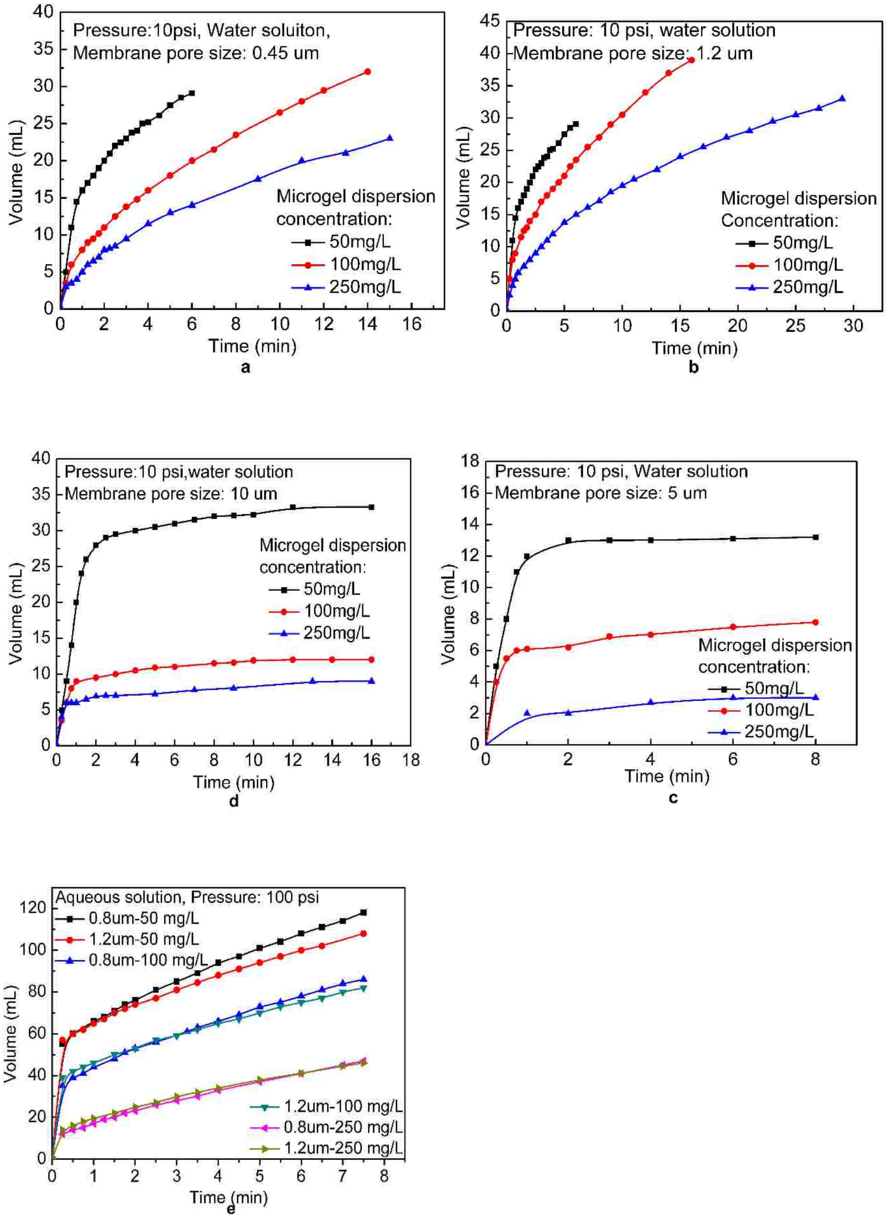

Figure 7. Nuclear-pore modeling of pore occlusion performance by microgel (a) Low pressure, membrane pore size: 0.45 µm; microgel/water dispersion with different concentration; (b) Low pressure, membrane pore size: 1.2 µm, microgel/water dispersion with different concentration; (c) Low pressure, membrane pore size: 5 µm, microgel/water dispersion with different concentration; (d) Low pressure, membrane pore size: 10 µm, microgel/water dispersion with different concentration; (e) High pressure, microgel/water dispersion with different concentration, membranes with small pore size.

For membranes with the larger pore sizes of 5 µm and 10 µm (Figure 7c and 7d), after the spurt loss, near zero flows were obtained indicating nearly complete occlusion of membrane pores. In these cases the gel particles performed efficiently in sealing the membranes with pores of size 5 µm and 10 µm though larger pore size membranes resulted in increased spurt losses compared to the smaller pore size membranes. Dispersions of lower microgel concentration also had larger volume spurt losses. Occlusion efficiency was proportional to gel concentration. A contrasting pore occlusion efficiency was observed when comparing smaller pore size verse larger pore size membranes with regard to average particle size. Microgels sealed pores generally larger and more widely spaced that diameters of the microgel particles better than pores smaller and more closely spaced compared to microgel particle size.

Higher pressure was used to test the sealing performance of 0.8 µm and 1.2 µm pore membranes. Behavior similar to lower pressure testing was observed (Figure 7e). After spurt loss, the flow of filtrate solution was constant, rendering a series of parallel curves. The microgels did not completely seal the membrane pores but reduced flow rate. The critical point in the flow slope verse time was smaller for more concentrated dispersions. As dispersion concentration was increased, a flow rate reduction occurred more quickly but the equilibrium flow rates were similar even for microgel dispersions of different particle size and dispersion concentration.

A discrepancy was observed between ability to occlude large pores compared to small pore membranes. Our first hypothesis was that the microgel particles, especially smaller ones, should be extruded through the larger nuclear pores and pass through the membrane with filtrate during the test but should be effective in occluding smaller pores.[12,53] However, we did not, observe occlusion of smaller pores. To test our particle extrusion hypothesis, the dispersions before the pore occlusion test and the filtrate solutions were compared. Dispersions were concentrated by centrifugation and observed using a microscope.

Spherical particles were observed in the dispersion before filtration with an average microgel diameter of about 35 μm with a Gaussian distribution. No microgel spheres with diameter larger than 1 μm were detected in the filtrate. We also observed that nearly all gel particles were retained by the membrane. Membranes with larger pore size have fewer pores and increased separation distance between adjacent holes in the film. Membranes with smaller pore size, in contrast, had a compact distribution.

A similar discrepancy was observed by Hua et al.[22,30,31] After preparing a polydisperse microsphere emulsion through water-in-oil emulsion polymerization, the average size of their swollen microgel particles employed in the filtration test was around 50 μm. The water-swollen microgels were injected through membranes under pressure of 0.05MPa (7.25 psi). Almost no pore occlusion effects were observed when testing membranes with the pore sizes smaller than 7 μm but the filtration rate decreased slightly as diameter of the pore increased to 7 μm. Occlusion was then observed when a membrane of pore diameter 10 μm was tested.

We propose the following occlusion model (Figure 8). A membrane of smaller pore size and spacing (1.2 μm) than microgel particles is shown in Figure 8a. The distance between adjacent holes and flow through the holes per surface area are too small to hold one gel particle to the filter surface. The larger, steric diameter of one gel microsphere will cover several pores; however, most pores remain unconcluded with

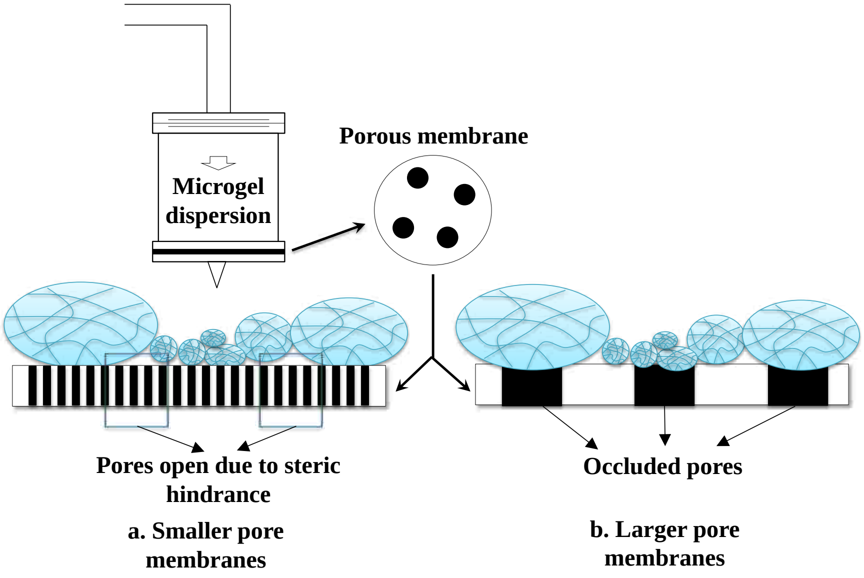

Figure 8. Schematic diagrams of pore occlusion mechanisms for membranes with smaller and larger pores compared to average gel particle sizes.

interstitial flow between particles. In our pore occlusion tests, upon microgel dispersion injection the gel particles formed a film on the top of membrane but there was not effective occlusion performance for pore membranes smaller than particles.

Figure 9 shows SEM pictures of membranes recovered and observed after pore occlusion testing. While the original swollen microgels were saturated with water, the microgel particles flattened upon drying. Adjacent gel particles in the SEM images support steric hindrance of pore access by neighboring gel particles, which prevented more gel particles from occluding pores. Sterically limited access allowed higher flow through narrow pore membranes than larger, widely spaced pores compared to particle size. Thus the gels were most effective at occluding pores of size similar or larger than particle diameter, as observed by others.[22,30,31] The observation is significant toward supporting the inability of larger particles to occlude smaller pores, which can prevent damage in oil well flow fields.

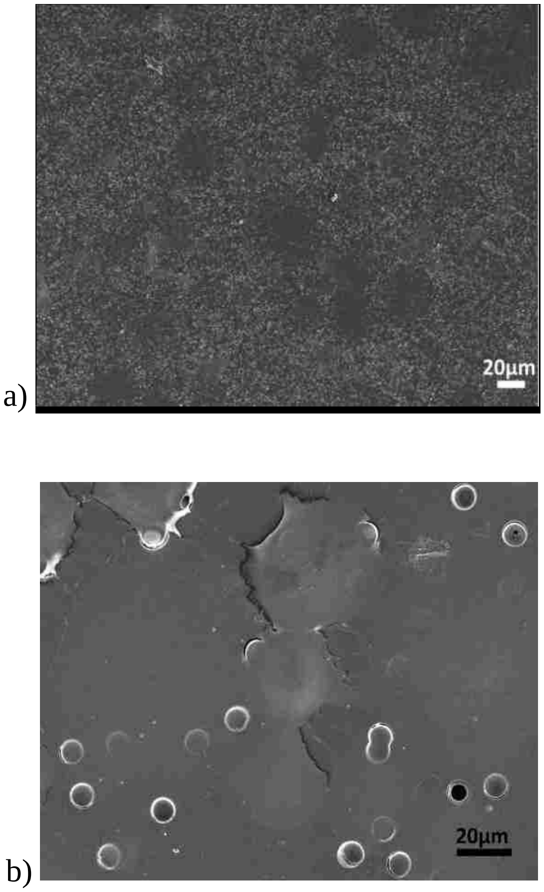

Figure 9. SEM Picture of membranes after pore occlusion testing. a) membrane with nuclear pore size of 1.2 µm; b) membrane with nuclear pore size of 10 µm.

CONCLUSIONS

A new water-free synthesis method was developed to polymerize polyacrylamide microgel above the melting point of the monomer. Little surfactant (2 wt.-% Span 85) was required in the synthesis and solvent was recyclable to reduce production cost. The produced gel particles were dry microspheres and readily dispersed in water. Comparable, microgels synthesized by traditional methods require post-treatments, like grinding and dehydrating, to produce dry powder gel particles.

In this paper, two different crosslinkers were employed to give the synthesized particles thermally responsive properties with two stages of aqueous size expansion. The average diameter of the microspheres was 7 μm. After fully swollen in water at room temperature, the microgel's average diameter had increased to about 20 times the original size. At a higher temperature stimuli of 80 ℃, the average volume of the water saturated microgels swelled to 160 times larger than the original volume. The higher temperature induced cleavage of the labile PEGMA crosslinker but also stable crosslinker and/or induced chain scission, which was observed as a cyclic dimer molecule. During the process from synthesis through dispersion and water absorptive swelling, the shape of the microgel particles was spherical.

Pore occlusion performance of the microgels was studied by a membrane model. The relationship between the microgel particle size and the membrane pore size as well as the membrane pore separation density were important factors for occlusion efficiency. If the size of gel particles was much larger than the pore size and the pitch of pores, they did not produce effective occlusion of filtrate flow. The lack of efficiency appears to be due to steric hindrance of adjacent particles preventing occlusion of nearby pores. Swollen microgels sealed the nuclear pores with effective pore occlusion when size matched and of average size similar to or smaller than the membrane pores and pore separation.

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IV. Synthesis, characterization and evaluation of polyacrylamide /poly (vinyl alcohol) inter-penetrating network hydrogel for oil Recovery

Zun Chen,[1] Thomas P. Schuman,[1] Yifu Long,[2] and Baojun Bai[2]

[1] Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65401

[2] Department of Petroleum Engineering, Missouri University of Science and Technology, Rolla, MO 65401

Abstract

Hydrogels have been applied in many fields but poor mechanical strength has limited further development. In this article, a biocompatible higher strength hydrogel comprised of an interpenetrating network (IPN) of polyacrylamide (PAM) and poly(vinyl alcohol) (PVA). The hydrogel was synthesized by an in situ free radical solution polymerization with crosslinking of acrylamide with N, N′-methylene-bisacrylamide comonomers, as well as a chemical crosslinking of PVA with glutaradehyde. The composition of the PAM/PVA IPN hydrogels was characterized by Fourier transform infrared spectroscopy (FTIR) and the morphologies were observed by scanning electron microscopy (SEM). The investigations of the hydrogels' swelling kinetics in brine demonstrated that the PAM/PVA IPN hydrogels had less sensitivity to salt and pH than a neat PAM hydrogel. The formation of a PVA network decreased the equilibrium swelling ratio (SR) of hydrogels; however, it greatly increased the mechanical properties of hydrogels. Incorporating from 2 wt% to 15 wt% of PVA into hydrogels' network, both storage modulus and loss modulus were enhanced and cracking stress was enhanced from 25 to 60 times as much as the control, neat PAM hydrogel. Yield stress was promoted from around 140 Pa for the control PAM hydrogel to over 800 Pa for a PAM-PVA IPN. The mechanical crosslinking by the IPN structure resulted in better mechanical performance by PAM/PVA IPN hydrogels.

Keywords

Poly (vinyl alcohol), Polyacrylamide, Inter-penetrating network, Swelling kinetics, Rheology, Mechanical Properties

Introduction

Hydrogels feature a three dimensional polymer network structure that can absorb, swell and retain aqueous solutions up to hundred times their original weight and volume.[1, 2] Generally, they are water soluble polymers loosely crosslinked by ionic, organic crosslinkers and/or physical crosslinking points to form three dimensional network structures. Hydrogel properties such as mechanical [3], thermal, optical,[4, 5] electrical,[6, 7] and responsiveness [8, 9] behaviors can be tunable by adjusting composition and crosslinking density. These properties enable hydrogels for a variety of applications in: flocculents or scavenging agents,[10, 11] drug delivery agents,[12-14] bio-compatible tissues,[15, 16] sensors,[9, 17, 18] oil recovery [19-21] and other areas.[22] Polyacrylamide (PAM) hydrogels are one of the most important hydrogels used in these areas.

In enhancing oil recovery (EOR) applications, PAM hydrogels have become a commonly utilized plugging agent/diverting agent toward conformance control, which is ascribed to their relatively low cost, non-toxicity and biological inertness, long polymer chain length and high molecular mass, stability of mechanical and morphological properties, and ability to customize their properties.[23, 24] Bai et al. has researched [21, 25-28] polyacrylamide preformed particle gels (PPG). Lab and field experimental results support use of PPG treatments as cost-effective methods for treating permeability and flow heterogeneity issues in petroleum reservoirs with fractures or void space channels, each of which are widely found in mature water-flooded oil fields.[19, 29]

Under stimuli of acid or salinity, on the one hand, PAM hydrogels display dramatic shrinkage in size due to ion shielding effects.[30, 31] On the other hand, highly swollen PAM hydrogels are generally brittle since they are lack of an efficient energy dissipation mechanism arising from an irregular distribution of crosslinking points.[32, 33] These drawbacks have limited PAM hydrogels’ applications under some circumstances. Improving the mechanical properties of PAM hydrogels is one potential means to expand their application. Compared to PAM gels, PVA hydrogels are another, inexpensive material which has low toxicity, good bio-compatibility[34] but lower hydrophilicity. Most importantly, PVA has better resistance to pH-changes, salinity, temperature and higher mechanical strength capability. When incorporated into other polymer hydrogels, PVA has the capability to improve their mechanical properties [35] as an environmentally friendly modifier. PVA has been incorporated into PAM hydrogels to make PAM/PVA composition, and achieved improvements in acid and salt- resistance as well as mechanical strength, demonstrating that PVA hydrogels can function well in harsh acidic or briny environments.[36-38]

Two methods have been reported to incorporate PVA into hydrogel polymer networks: (1) Polymerizing or crosslinking water soluble monomers or polymers in PVA solution.[39, 40] In this method, water soluble monomers or polymers and their crosslinker were dissolved in linear PVA solution and an in-situ polymerization and crosslinking reaction results after adding initiator. The synthesis is a physical mixing initially that, through polymerizing and crosslinking acrylamide, incorporates linear PVA into a gel matrix[41] without further crosslinking as semi-interpenetrating networks or semi-IPN.[42] (2) Polymerizing or crosslinking water soluble monomers or polymers in PVA solution, following by a freeze-thaw associative crosslinking of PVA.[43, 44] Compared to the first network example, the freeze thaw method provided a second network via creating hydrogen bonds as associative crosslinking points between PVA polymer chains. The associative IPN was stable in moderate temperature or shear environments due to disruption of hydrogen bonding under elevated temperature (45~55 °C) or shear.[45, 46] When these stimuli are applied, the associative crosslinking points may dissociate to form a semi-IPN. For semi-IPN PVA could be released into the environmental aqueous solution.

In this experimental study, a series of PVA/PAM IPN hydrogels containing various amounts of PVA were prepared by in situ free radical solution polymerization of AM and MBAM, as well as a chemical crosslinking of PVA by glutaraldehyde [47,48]. Production of the IPN versus a semi-IPN entanglement[41] or associative hydrogen bonding crosslink, by covalent bonding between PVA polymer chains should provide a more stable network under aqueous swelling and shear. An IPN of PAM and PVA is intended to improve the mechanical properties of the swollen three dimensional IPN. The swelling performance of the hydrogels as a function of salt concentration and different pH were measured. Rheological and mechanical properties are determined and discussed.

Materials and methods

Materials

Preparation of poly (vinyl alcohol)/polyacrylamide interpenetrating network hydrogel was carried out with commercially available monomers, initiators, and reagents. The monomer used in preparing the primary network was acrylamide (AM, ≥98.0%, Alfa Aesar). Poly(vinyl alcohol) (PVA, molecular weight:78000 g/mol, 98.0% hydrolyzed, Sigma Aldrich) was used for formation of the second network; N, N′-methylene-bisacrylamide (MBAM) (~99%, Sigma Aldrich) and glutaraldehyde (Grade II, 50 wt% in H_2O, Sigma Aldrich) were employed as crosslinkers for AM and PVA respectively. Ammonium persulfate (APS, ACS reagent, ≥98.0%, Sigma Aldrich) was used as initiator. Hydrogen chloride (HCl, Technical, Fisher Chemical) and sodium hydroxide (NaOH, Fisher Chemical) were used to adjust pH. Sodium chloride (NaCl, Fisher Chemical) was used to prepare aqueous brine. Potassium bromide powder (KBr, ACS reagent, ≥99.0%, Fisher Chemical) was used as a window material for Fourier transform infrared spectroscopy.

Synthesis

The PVA/PAM double network hydrogel was synthesized via chemically crosslinking PVA linear polymer in presence of free radical solution polymerization and crosslinking of acrylamide in a 100 mL glass bottle. By changing the weight ratios (0, 2, 10, or 15 wt.-%) of PVA, a designed amount of PVA powder was fully dissolved in DI water under magnetic stirring, at temperature of 90±5 ℃. PVA solution was let to cool down to room temperature, then 30 g AM monomer and 0.17 wt.-% MBAM (based on AM) were added into PVA solution. After completely dissolving, the systematic pH was adjusted to3 using 3M HCl. The solution mixture was purged with argon for 30 min. to dioxide. A 0.05 wt.-% of APS (based on AM) and 0.1 wt.-% of glutaraldehyde (based on PVA) in water solution were added into system and stirred for 1 min to a uniform solution. Placing the reaction bottle at room temperature overnight, a semi-transparent double network PVA/PAM hydrogel was collected. Crude, semi-wet bulk gels were cut into designated size and dried prior to evaluation. A series of PVA/PAM interpenetrating hydrogels were prepared with different PVA content.

Characterization

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the powder samples were recorded on a Nexus 470 FT-IR (Thermo Electron Corp.). Particle gels were vacuum dried overnight at 60 ℃ and 10mmHg. Dried particle hydrogels samples were diluted by mixing dry polyacrylamide microspheres with KBr at about 1:100 (wt/wt) ratio. Spectra were collected at 2 cm^{-1} resolution in mid-IR region (4000–400) cm^{-1}.

Scanning electron microscopy (SEM) study

SEM was performed using a Helios Nanolab 600 FIB scanning electron microscope. Swelled hydrogels were cut into small pieces and freeze-dried to keep their original network structures. The dried hydrogel-networks were directly mounted using conductive tape to a stainless steel SEM stub, and sputter coated with Au/Pd. SEM imaging was conducted using a field emission source at a 5kV accelerating voltage and 43 pA current at a working distance of 3 to 6 mm with an Everhart-Thornley detector.

Swelling properties of PVA/PAM IPN hydrogels

Dried crude hydrogel was cut into particles of size 20 to 30 mesh (0.60 to 0.84 mm). These particles were placed into a conical graduate cylinder with volumetric scale. Dry particles' volume was measured and immersed into brine of a specific salt concentration to absorb water and swell. The swollen volume of the PVA/PAM IPN was measured under room temperature (25 ℃). The same procedure was repeated for the solutions of different pH values (2 to 7), which was adjusted by aqueous HCl and NaOH solutions. The swelling ratio (SR) was calculated by the following equation:

$$SR=V_s/V_d \qquad \text{Equation 1}$$

where V_s and V_d are the measured volumes in their swollen and dry states, respectively.

Rheological and mechanical properties of PVA/PAM IPN hydrogels

Rheological measurements were carried out with Haake Marsi II Rheometer (Germany) with a parallel-plate system PP35-Ti under ambient temperature (25 ℃) with 'gel disc' model. Detailed procedures follow the method of Bai, et al.[49] In this study, two predominating methods were involved, dynamic rheological measurement (DRM), focused on oscillatory shear, and static rheological measurement (SRM) featuring unidirectional, constant rotational shear. Samples were prepared by cutting the swollen bulk gels into 8 x 8 x 3mm cubes.

***Dynamic Rheological Measurement**:* In DRM, an amplitude sweep is a common method consisting of dynamic stress sweeping and oscillatory frequency sweep testing. The dynamic stress sweep was carried out with a stress range from 0.1 Pa to 10000 Pa at a fixed frequency of 6.28 rad^{-1} (i.e., 1 Hz). The oscillatory frequency sweep measured resistance stresses over a frequency range of 0.01 to 100 rad^{-1} (from 0.00159 to -15.9 Hz) in oscillation mode.

***Static Rheological Measurement**:* The steady stress sweep was carried out with a stress range from 2 Pa to 2000 Pa and maintained for 180 s. Through SRM, a yield stress τ_y was determined, defined as the minimum stress required to initiate flow.

Results and discussion

Structure and morphology of PVA/PAM IPN hydrogel

A series of PVA/PAM IPN hydrogels over a range of PVA contents were prepared by in-situ free radical solution polymerization of AM and MBAM, with a concurrent chemical crosslinking of PVA. The composition of the IPN hydrogels is listed in Table 1. The representative crosslinking structures are proposed in Figure 1. The first network contains polyacrylamide crosslinked by N’N-methylene bisacrylamide (Figure 1a) whereas the second network is obtained by a crosslinking of poly(vinyl alcohol) by glutaraldehyde under an acidic environment (Figure 1b).[47,48]

Table 1 Composition of PAV/PAM IPN

Samples	PVA (g)	AM (g)	MBAM (g)	Glutaraldehyde (g)	Water (g)
Pure PAM	0	30	0.05	0	70
2% PVA/PAM	0.6	30	0.05	0.0006	69.3
10% PVA/PAM	3	30	0.05	0.003	67
15% PVA/PAM	4.5	30	0.05	0.0045	65.4

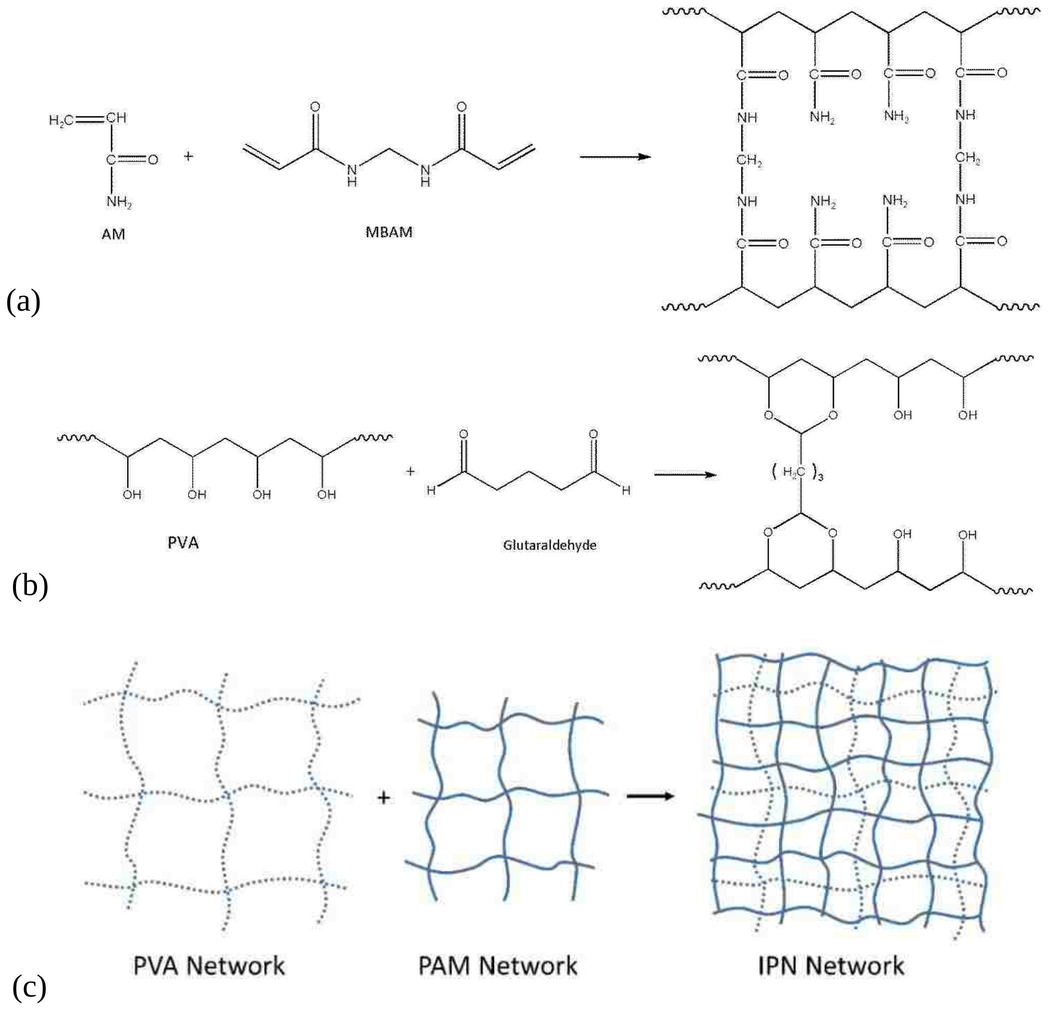


Fig. 1 (a). The first network: polyacrylamide with N, N-methylene bisacrylamide as crosslinker; (b). The second network: poly (vinyl alcohol) –glutaraldehyde; (c). The representation of interpenetrating network of PAM/PVA

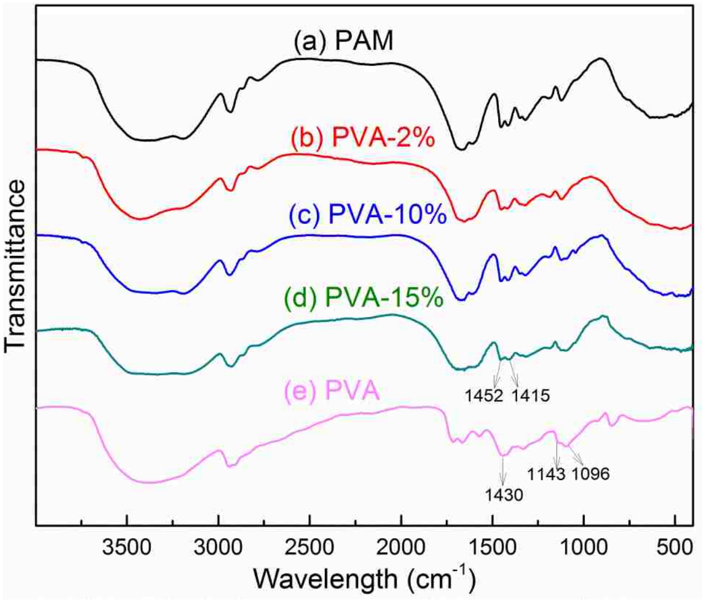


Fig. 2 FTIR of (a) Pure PAM;(b) PVA-2%/PAM IPN; (c) PVA-10%/PAM IPN; (d) PVA-15%/PAM IPN; (e) Pure PVA

Infrared spectroscopy is a useful technique in characterizing composition of materials. Figure 2(a) indicates the spectrum of pure PAM; Figures 2(b) thru (d) display the spectra of PAM/PVA IPNs of different PVA concentration; and Figure 2(e) shows the bands of PVA. A broad absorption band at 3395cm^{-1} and 3198 cm^{-1} are due to stretch vibrations of the N-H group. The characteristic peaks at 1670 cm^{-1} , 1415 cm^{-1} are vibrations of the C=O (amide I) and C-N, respectively. The absorptions at 2940 cm^{-1}, 2863 cm^{-1} and 1450 cm^{-1} reflect the vibrations of -CH$_2$-. In the spectrum of pure PVA, 3360 cm^{-1}, 1441 cm^{-1}, 1096 cm^{-1} are due to the vibrations of the O-H and C-O of secondary alcohol. In the case of PAM/PVA IPNs, the absorption at 1430 cm^{-1} split into two bands at 1451 and 1415 cm^{-1}, and the peak at 1096 cm^{-1} moved toward lower frequency. A new absorption band due to C–O–C stretching vibration at 1179 cm^{-1} appears. The appearance of the ether group is assigned to intermolecular and intramolecular self-crosslinking.[41] It should be noted that the crystallization-associated band of PVA at 1143 cm^{-1} was not present in FTIR spectra of PAM/PVA IPNs, supporting the transition of PVA from crystalline to amorphous structure.[36, 38, 50]

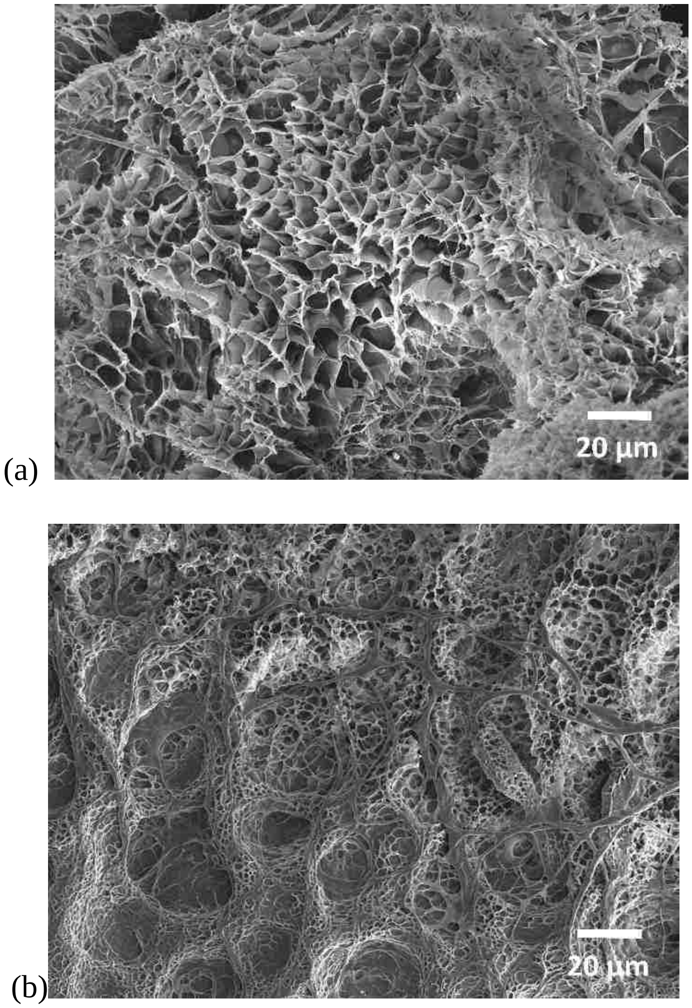


Fig. 3 Scanning electron micrographs of PAM hydrogel and PAM/PVA IPN hydrogel.(a) PAM hydrogel network; (b) PAM/PVA (10%) IPN hydrogel. The PVA appears as less porous ropes dispersed within surrounding porous PAM hydrogel

Porosity correlates with mechanical performance of a polymer matrix and affects the ability to apply the polymer, e.g., in the encapsulation of other materials. The as-synthesized PAM network hydrogel and PAM/PVA IPNs had highly porous structures upon freeze drying (Figure 3), which would suggest effective absorption of water. The pore diameters of PAM (Figure 3a) were reduced in size as the secondary polymer network was added (Figure 3b). The SEM micrographs clearly illustrate different morphology when PVA was added into system. From Figure 3b, the IPN gels exhibited an obvious secondary network. In their work on PAM/PVA semi IPNs, Mishra et al. [40, 42] reported linear PVA polymer without further crosslinking was observed embedded into the polyacrylamide network. However, no obvious porous structure was observed in their SEM micrographs.[51]

Rheological and mechanical properties of PAM/PVA IPN hydrogel

In order to determine the information about the rheological and mechanical properties of the IPN hydrogels network we subjected the hydrogels (swelled in 1 wt. % brine) to shear stress applied by a HAAKE MARSIII rheometer.

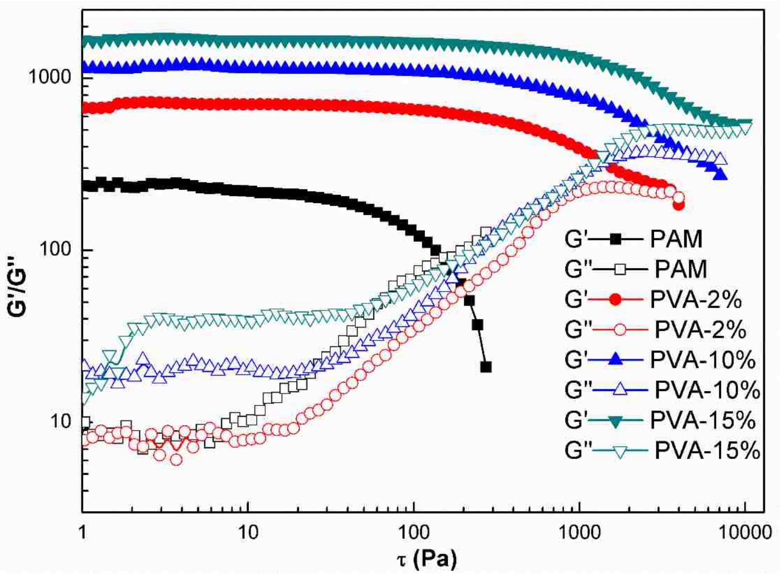


Fig. 4 Elastic (G') and viscous (G") moduli vs. oscillation frequency measured in a stress sweep test. The cross-over point (G' = G") represents the point of crack stress (S_c)

The trends of storage or elastic modulus (G') and the loss or viscous modulus (G") vs. oscillation stress frequency for PAM and PAM/PVA IPNs are shown in Figure 4 as a function of PVA concentration. At low oscillation frequency, the elastic moduli (G') are higher than the viscous modulus (G") indicating the gel-like nature of the material, which indicated that elastic behavior of the sample predominates over its viscous behavior. The swollen samples at low frequency shear exhibited mechanical rigidity and displayed reversible stretching. Beyond the crossover point, i.e., at the oscillation stress where G' and G'' are the same value, the viscous modulus trends higher than the elastic modulus, which is characteristic of a liquid. Above the crossover point the gel's viscosity dominates over elasticity behavior. In this range, the shape change of the hydrogels became destructive and irreversible, thus the intersections indicate the crack stress (S_c) of the hydrogels. The crack stress of the IPN hydrogels was dramatically increased with an increase in PVA concentration (Table 2).

Table 2 Properties of hydrogel

Hydrogel	Crack Stress (S_c, Pa)	Ave. G'(Pa)	Ave. G"(Pa)	G* (Pa)	Yield Stress (τ_γ, Pa)
PAM	153	237.2	14.2	237.6	141
PVA-2%	2495	692.7	17.1	692.9	402
PVA-10%	3960	1294.2	36.5	1294.7	570
PVA-15%	7080	1893.7	62.4	1894.7	703

Complex modulus: $G^* = \sqrt{G'^2 + G''^2}$

The linear viscoelasticity of the PAM, PAM/PVA IPN hydrogels was also determined through measuring G' and G'' as a frequency sweep experiment (Figure 5). In a linear viscoelastic range (LVR), microstructure of the hydrogels is theoretically maintained; hence, deformation of the hydrogels are non-destructive, reversible, and reproducible. A linear viscoelastic response was confirmed over the range of frequencies by constant G’ and G’’ over the range of frequencies used.

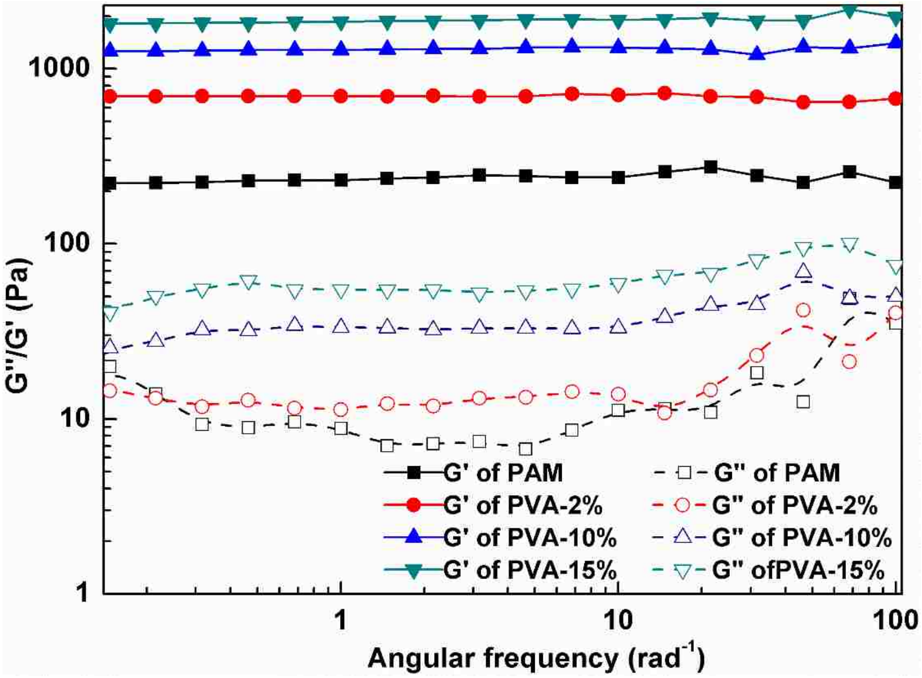


Fig. 5 Influence of frequency on the elastic modulus (G’) and viscous modulus (G’’) of PAM hydrogel and PAM/PVA IPNs.

A frequency sweep experiment of the pure PAM hydrogel and the PAM/PVA IPNs (Figure 5) was performed under constant maximum applied stress in the LVR. At the frequency of 1Hz (= 6.28 rad^{-1}) both G’ and G’’ were significantly enhanced compared to neat PAM hydrogel values upon increasing the concentration of the secondary PVA network. In earlier work, HPAM/PVA semi IPN (of 10 wt.-% PVA) had reported average G’ of about 45 Pa and an average G’’ of 25 Pa.[39] In comparison, the double network PAM/PVA IPNs exhibited superior elastic modulus advantages, gradually increasing with PVA concentration and having a G' over 1 kPa and G" of about 30 Pa for the 15 wt.-% PVA concentration IPN.

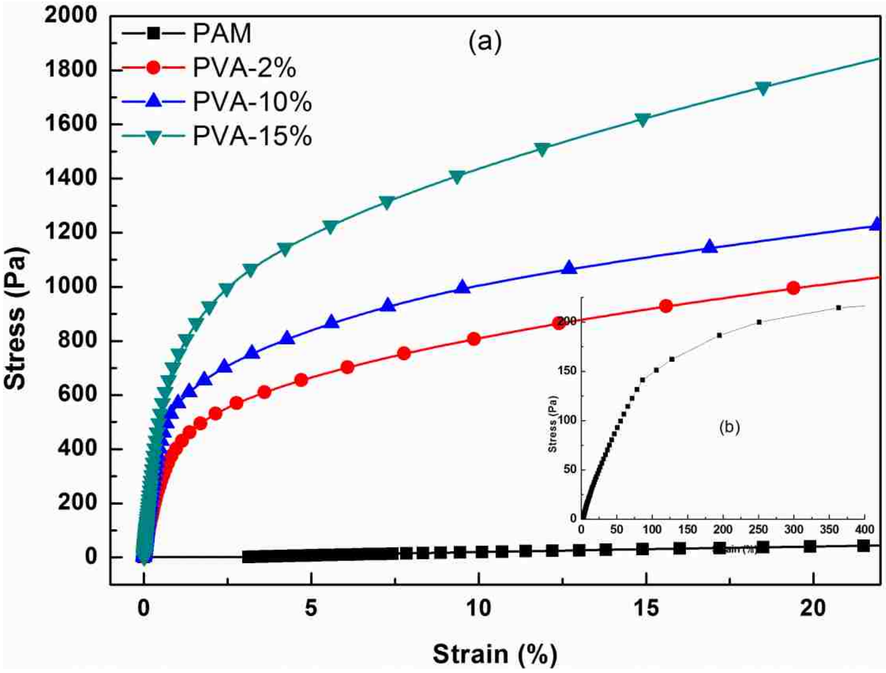


Fig. 6 (a). Strain-stress curves of PAM hydrogel and PAM/PVA IPNs; (a). Expanded strain-stress curves of PAM hydrogel

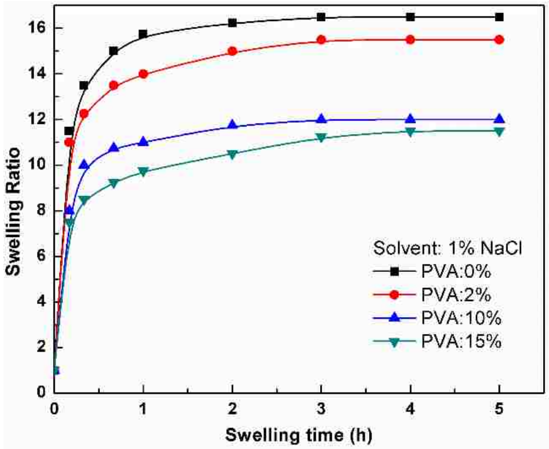
Through rheological measurement, the yield or as also referred to tensile strength (τ_y) for the gels was determined. Yield strength is defined as the stress at which a material begins to deform plastically. Figure 6 shows stress-strain curves measured as a function of applied strain in swollen disc samples. The loading of PVA readily enhanced the yield stress of hydrogel from around 141 Pa for pure PAM to 703 Pa for the IPN with 15% PVA concentration (see also Table 2).

The determination of yield stress is of special significance in EOR.[25] As a plugging agent, the gel is desired to resist flow through subterranean fractures or porosity. The yield stress of the gel is characteristic of the minimum pressure gradient necessary to cause gel deformation and flow[31, 37] and has been correlated with the measured yield stress.[30] We observe that upon incorporating a PVA network into PAM as PAM/PVA IPNs, the mechanical properties of these composite gels and resistance to flow through pores should be significantly improved, by about a factor of 5. [52]

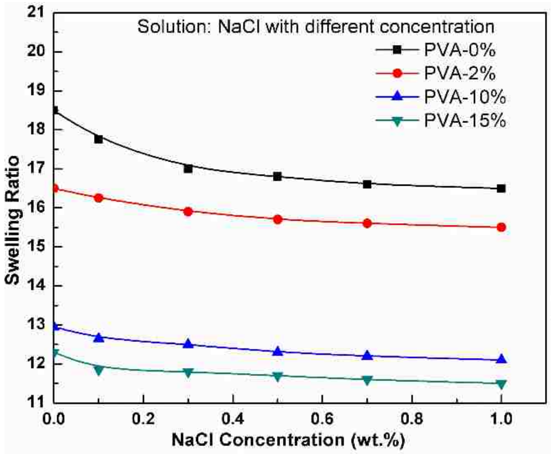
Swelling behavior of PVA/PAM IPN hydrogels

Swelling performance is one of the most crucial properties of hydrogels. Hydrogels' swelling behaviors in pure water have been extensively studied.[53-55] Generally, almost all the hydrogels exerted better water-absorbing capacity in pure water than in brine solutions. However, it is also important to measure the swelling behavior of gels in different types of salt solutions for many situations, e.g., as may occur in an enhanced oil recovery (EOR) application. Almost all EOR working environments utilize formation water, which generally contains multivalent ions as portion of an overall high aqueous salt concentration. The characterization of swelling capacity for the PAM/PVA IPNs were conducted in (a) 1 wt.-% NaCl solution; (b) brine water as a function of salt concentrations; (c) 1 wt.-% NaCl solution over a range of pH as adjusted using HCl solution (Figures 7a, 7b, and 7c).

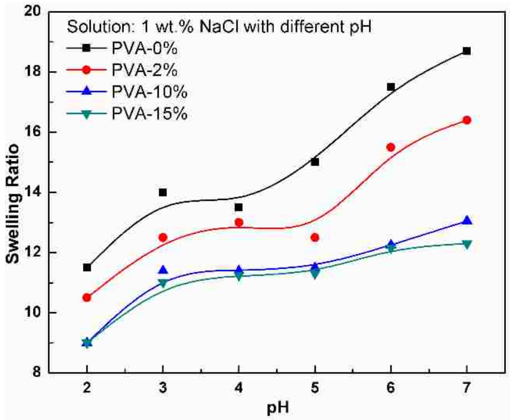
The swelling kinetic of the PAM gels, and PAM/PVA IPN gels in 1% NaCl are displayed in Figure 7(a). Neat, non-ionized PAM hydrogel was employed as a control in our study (swelling ratio (SR) = 18.5 in pure water). Neat PAM gel swelled much less compared to a partially hydrolyzed PAM (HPAM) hydrogel with a degree of hydrolysis of 20~25% (SR = 50 in pure water) [39]. With increasing PVA content, the equilibrium



(a) a. Swelling kinetic in 1wt.%NaCl



(b) b. Swelling ratio vs. salt concentration



© c. Swelling ratio vs. pH

Fig. 7 The swelling behavior of the PAM/PVA hydrogels. (a) The swelling kinetics of the PAM/PVA IPN hydrogels with different PVA concentration (0%, 2%, 10%, 15%) in 1% NaCl at room temperature. (b) The effects of salt concentration on swelling behavior of PAM/PVA IPNs at room temperature. (c) The swelling kinetics of the PAM/PVA IPN hydrogels in 1% brine water as a function of pH (2~7) adjusted by HCl at room temperature swelling capacity of the hydrogels was decreased. While the PVA chains contain polar protic hydroxyl groups that render the PVA gel network swellable in an aqueous environment, crosslinked PVA networks did not swell as much as PAM hydrogel. The PVA interpenetrating network appears to restrict the swelling of PAM network. As the content of PVA increased, this constraint effect was increased to further restrict the swelling of the PVA network. However, the IPNs' swelling kinetics were similar to the PAM gel control, reaching equilibrium in about 1 hour.

Figure 7(b) indicated the effect of different salinity concentrations on swelling ratio. Non-ionized PAM hydrogel swells much less than hydrolyzed PAM (HPAM) hydrogels.[39, 56-58] The slightly larger upturn in swelling ratio for the IPNs with less PVA concentration suggest some hydrolysis to an acrylic acid repeat unit, making the polyacrylamide chains per-se slightly sensitive to salt concentration but slightly less sensitive to increasing salt concentration with increasing PVA concentration. Overall swelling ratio is still decreased by increased PVA concentration. For the control PAM gel network, the percentage change in swelling ratio was 8% when salt concentration reached to 0.3% and an additional 3% change at 1% brine. For hydrolyzed PAM hydrogels, the percentage of SR reduction could be well over than 40%, up to 80% [39, 56-58] in brine.

There are several reasons for observed reductions in swelling volume by PAM gels. If the PAM possesses hydrolyzed PAM repeat units, which is chemically equivalent to copolymerization of acrylamide with acrylic acid, an ion-shielding effect reduces chain-chain repulsion. Therefore, a volume collapse occurs upon increasing the ionic strength of the aqueous solution. A second, related effect is that of pH, where the repulsion between polymer chains created by dissociated carboxylate anions is similarly reduced by protonation of the carboxylate to the free acid by strong acid as used to control pH. Since the swelling ratio as a function of pH was performed in 1% brine, the increase in ionic strength should be minimal with respect to the effect of pH regarding the trend provided in Figure 7(b).

For PAM/PVA IPN gels, the swelling of the second, crosslinked PVA network restricts swelling of the acrylamide network. While PVA swelled less in pure water, it was also less affected in swelling extent by the increase of salt or a reduction in pH (see Figure 7(c)). One concern in acidic solution was the sensitivity of the glutaraldehyde crosslinking, whose (hemi-) acetals would hydrolyze in acid and break the PVA network. The hemiacetal hydrolysis would result in a semi-IPN network as described above and in [39,41,42] except where cleavage of the MBAM occurs.

Swelling kinetics of semi-HPAM/PVA IPNs were reported by Jamal Aalaie, et al.,[39] who prepared semi- IPNs by crosslinking HPAM (degree of hydrolysis: 20 to 25 mole %) with chromium triacetate in PVA solution. Upon increasing the concentration of PVA, their semi-IPNs' SRs were decreased similar to our result. However, their semi-IPN with 10 wt. % PVA of initial swelling ratio 48 shrank over 40% in volume when subjected to 0.5 wt.-% brine. In comparison, the volume loss for our PAM/10 wt%-PVA IPN hydrogel of initial swelling ratio 13 was 6.56%. Compared to the semi IPN approach, our two network IPNs had less percentage volume shrinkage in brine due to the fully government of secondary PVA-network. However in semi-IPN network, the crosslinking of PVA is caused by polymer chain entanglement and the linear PVA can move as the swelling of PAM network.

Compared with traditional PAM hydrogels, the swelling properties of the PAM/PVA IPN hydrogels in this work were reduced but the swollen gels were much stronger mechanically. Change in SR and mechanical strength were especially dependent on the amount of PVA. Where practical application can tolerate a lower swelling ratio but requires greater mechanical strength, a dual IPN PAM/PVA gel would appear to be a viable candidate.

Theory description

The swelling behavior of the hydrogels was analyzed within a framework of the Flory–Rehner theory of swelling equilibrium, including the ideal Donnan equilibria. According to the Flory–Rehner theory, the osmotic pressure π of a gel is the sum of three contributions [59, 60].

$$\pi = \pi_{mix} + \pi_{el} + \pi_{ion} \qquad \text{Equation 2}$$

where π_{mix}, π_{el}, and π_{ion} are the osmotic pressures due to polymer–solvent mixing, due to deformation of network chains to a more elongated state, and due to a non-uniform distribution of mobile counter-ions between the gel and the solution, respectively. In our study, nonionic monomers were employed in preparing our hydrogels. Additionally, to consider if the IPN hydrogels are sensitive to salt (see Figure 7b), the assumptions were: i) while Na+ and Cl- ions are small enough to pass through the porous hydrogel network, at equilibrium state we assume the change in non-uniformity of counter-ions should be small enough to be negligible, i.e., $\pi_{ion} \approx 0$, and ii) added salt affected the swelling of pure PAM network through changing χ_1, the polymer–solvent interaction parameter, to make the PAM network shrink. Related to π_{ion}, the χ_1 as a function of the ionic strength of the solution is not readily expressed by solubility parameter. From this point of view the polymer-solvent interaction parameter, χ_1, is assumed to change and accounts for changes in SR ratio. The incorporation of the PVA network, if less affected in its solubility, may constrain as well as sustain the SR of the PAM network in low and high ionic strengths, respectively.

To simplify calculation, only π_{mix} and π_{el} were considered in studying the swelling kinetic of the IPN hydrogels in 1 wt.-% NaCl. At equilibrium, the total osmotic pressure (π), which is the sum of osmotic pressures from mixing (π_{mix}) and network elasticity (π_{mix}), must be zero [60, 65] and $\pi_{mix} = - \pi_{el}$ and will result in Equation 3, where ν is the strand density, M_c is average molecular weight between crosslinks, V_1 is the molar volume of 1 wt.- % NaCl solution (18.42 cm^3/mol), and v_2 is the average volume fraction of polymer in the hydrogel when it reaches the equilibrium swelling state. We assumed a value of χ_1 =0.48, which provided a good fit to the experimental swelling data of acrylamide-based nonionic anionic, cationic, and ampholytic hydrogels of various compositions.[61-64] The value of ν_2 is given by Equation 5, where $\rho_p$is the polymer density (1.13 g/cm^3), ρ_s is the density of 1 wt.-% NaCl solution (1.0053 g/cm^3 at 25 ℃) and SR is the swelling ratio of hydrogel..

$$\pi_{mix} + \pi_{el} = 0 \qquad \text{Equation 3}$$

$$\boldsymbol{v} = \frac{\rho_p}{M_c} = \frac{ln(1-v_2)+v_2+\chi_1 {v_2}^2}{V_1({v_2}^{\frac{1}{3}}-\frac{1}{2}v_2)} \qquad \text{Equation 4}$$

$$\boldsymbol{v_2} = (\frac{1}{\rho_p})/[\left(\frac{SW}{\rho_s}\right) + (\frac{1}{\rho_p})] \qquad \text{Equation 5}$$

The inverse of molecular weight per crosslink (ν_e) is defined as the crosslink density (Equation 6). From these equations we observe that a measured crosslink density is proportionally related to a change in χ_1, ν_2^2, and/or inversely related to SR^2 (Equation 7).

$$v_e = \frac{1}{M_c} \qquad \text{Equation 6}$$

$$v_e *= \frac{1}{M_c} \propto \chi_1 , \; \frac{1}{M_c} \propto v_2{}^2 \propto (\frac{1}{sw})^2 \qquad \text{Equation 7}$$

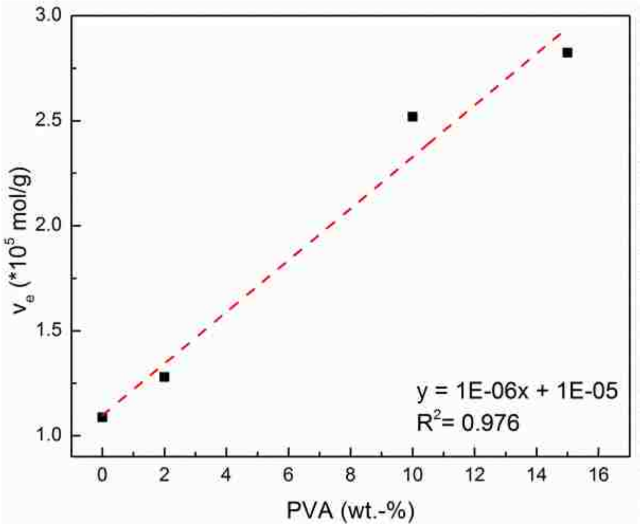


Fig. 8 Dependence of the effective crosslinking density (v_e) on the concentration of PVA

In this study, the PVA IPN was introduced as a secondary network. The PVA could then be considered as a crosslinker of PAM network. Figure 8 shows the relationship between the effective crosslinking density (v_e) and the concentration of PVA. We observe the data of v_e had a linear trend versus the gel IPN concentration of PVA. Here, v_e*is not considered as an absolute v_e, rather v_e* is determined by two factors: crosslink density and χ_1, each having a proportionality relationship with ν.

Therefore, to a certain extent, the loaded of PVA network could be considered as the contributor of crosslinking in the experimental situation. Additionally, it is well known that, network strength will increase with increasing crosslink density.[67,68] If so, there should be a proportional relationship between the loading of PVA and the IPN gel strength as well. The dependence of the complex modulus (G*) as a function of the loading of PVA was plotted in Figure 9. We observe an approximately linear trend between PVA content and elastic modulus. It could be concluded that, for PAM/PVA IPN hydrogels, the strength could be easily tuned by adjusting the loading of the secondary PVA network.

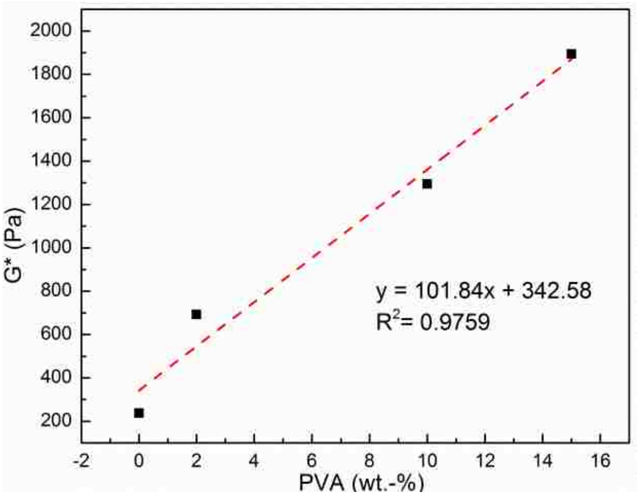


Fig. 9 Dependence of the complex modulus on the concentration of PVA

Conclusions

The objective of this work was to synthesize PAM/PVA IPNs as a high strength IPN of polyacrylamide and poly(vinyl alcohol) that could be applied in EOR water flooding. A series of PVA/PAM IPN hydrogels were prepared by in situ, free radical solution polymerization and crosslinking of AM with methylene-bisacrylamide, and concurrent crosslinking of PVA with glutaraldehyde. As a result of the secondary PVA network formation, the mechanical properties were greatly enhanced. Flory-Rehner theory was used to study the effect of loading of PVA on the swelling and mechanical properties of IPN hydrogel. It was shown that the concentration of the IPN in the hydrogel matrix was proportional to the obtained mechanical strength and swelling to custom design a product for specific application requirements. The potential of PAM/PVA IPN hydrogels for EOR was assessed by evaluating hydrogels swelling properties in brine and under stimuli of pH and salt concentrations. The PAM/PVA IPNs showed lower swelling ratios but also less sensitivity to salt and pH change than pure PAM hydrogel. Both PAM and PVA are biocompatible materials of low toxicity. The PAM/PVA IPN hydrogel products were observed to be highly porous in structure, which may also be suitable for potential tissue engineering and biomedical applications.

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SECTION

3. CONCLUSION

This dissertation has discussed the synthesis, characterization and application of polyacrylamides and polyacrylamide hydrogels.

Paper I mainly reviewed the function of polyacrylamide and its derivative products in EOR through two main aspects: one is the viscosity thickener as the polymer flooding agent; another is they can act as sealing agent via forming cross-linking structure in present of cross-linkers to render conformance control. This review clearly indicates the structure of the different polyacrylamide and their derivatives as well as the according properties of them. In particular, this review elaborates synthesis methods of each kind polymer and gives their application in detailed.

For the polyacrylamides working as the displacing agent, they work as a basic thickening agent in polymer flooding solution. As the reservoir environment turning harsher and harsher, a plenty of modification methods came up aiming at conquering the high temperature, high salinity, and harsh pH envrionment. Typically functional monomers have been summarized that could be employed to modify the polyacrylamide chain hence increase the solution viscosity facing different reservoir.

From the point of different crosslinking types, PAM hydrogels were reviewed aiming at the gel synthesis, mechanism of crosslinking, performance, lab evaluation and practical applications. This work will benefit A number of crosslinkers were summarized according to their type, properties and working conditions.

This paper mainly reviewed the PAMs based polymers and hydrogels utilized in EOR, highlighting the synthesis methodologies, structure and properties of the products as well as their real application in oil field, aiming at drawing more attention of chemists to this surging area of interest so that more advanced products could be developed to meet the tremendous demands for oil industry. In addition, polymers for EOR have been intensively applied in China and a lot of publications are in Chinese, and this paper will also benefit those who are not familiar with Chinese language.

In Paper II, a water-free, solvent-in-oil emulsion polymerization has been developed to synthesize polyacrylamides. The preparation of polyacrylamides has been conducted above the melting point of monomers in non-polar solvents. A number of surfactants had been studied in stabilizing this water-free system. Compared to traditional inverse emulsion polymerization, the water-free solvent in oil method consumed much less surfactant. Alkylacrylamides were employed as sufmer to stabilize the emulsion system as a surfactant and also polymerized into copolymer to introduce hydrophobic domain forming hydrophibically modified polyacrylamides. By virtue of this technique, the feed ratio of the hydrophobe will not be limited as it is in a traditional aqueous polymerization system. Products are dry powder and ready to use disperse in water, compared to traditional synthesis that require post-treatments, like drying, which increases energy cost. Additionally, dry powders are stable and easier to store and transport than wet polymer solution.

In Paper III, polyacrylamides microgel was synthesized by water-free, solvent-in-oil emulsion polymerization. Two different crosslinkers were employed to give the synthesized particles ‘smart’ properties with two stages of size expansion that are temperature sensitive. Original diameter of the microspheres was under 10 μm. After fully swelled in water under room temperature, the microgel's diameter had swelled to less than 20 times as the original size. While under higher temperature stimuli, the average volume of the saturated microgels swelled to over 150 larger than the original volume. High temperature could trigger the cleavage of labile crosslinker and some of the stable crosslinker. During the whole process, the shape of the microgel particles remained spherical. Plugging performance of the microgels was studied. There is a certain matching relationship between the microgel particle size and the pore size as well as the porosity. If the size of gel particles is much larger than the pore size, they will not produce effective occlusion due to steric hindrance. Swollen microgels sealed the nuclear pores with effective plugging, when size matched.

Paper IV described PAM / PVA inter penetrating network hydrogels, which showed much higher mechanical strength compared to pure PAM network and could be applied in gel treatment under harsh environment. IPN hydrogels were produced by crosslinking PAM-MBAM and PVA-glutaraldehyde at the same time in one aqueous system. Flory-Rhener theory was used to study the effect of loading of PVA on the swelling and mechanical properties of IPN hydrogel. It is shown that the IPN hydrogel matrix fabricated may easily be tuned in terms important parameters such as mechanical strength, swelling and porosity as per need by varying composition, thus fulfilling specific application requirements. PAM/PVA IPN hydrogels as plugging agent for gel treatment has been studied by evaluating hydrogels swelling properties in brine, under stimuli of pH changing and salt concentration. The PAM/PVA IPNs showed less sensitivity to salt and pH change than pure PAM hydrogel, which is preferred in EOR.

Both PAM and PVA are bio-compatible material, and meanwhile the PAM/PVA IPN hydrogels are of highly porous structure, which will be suitable for potential tissue engineering and biomedical applications.

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VITA

Zun Chen was born in Zhengzhou, Henan province in China. She obtained her Bachelor Degree in Polymer Science and Engineering and Master Degree in Materialogy from South China University of Technology in Guangzhou, Guangdong province in China in 2007 and 2010. She then attended Missouri University of Science and Technology (formerly the University of Missouri - Rolla) in Jan. 2011, and began her doctoral study under the guidance of Dr. Thomas P. Schuman. Her researches focused on polymer synthesis and characterization. In in December 2016, she received her Ph.D degree in Chemistry from Missouri University of Science and Technology, Rolla, USA.