Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–11

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Star-like hydrophobically associative polyacrylamide for enhanced oil recovery: Comprehensive properties in harsh reservoir conditions

Rui Liu[a,b,*], Wanfen Pu[a,**], James J. Sheng[a,b], Daijun Du[a]

[a] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, People's Republic of China
[b] BoL L. Herd Department of Petroleum Engineering, Texas Tech University, P. O. BOX 43111, Lubbock, TX 79409, USA

ARTICLE INFO

Article history:
Received 21 June 2017
Revised 24 August 2017
Accepted 26 August 2017
Available online xxx

Keywords:
Nano-silica particles
Star-like hydrophobically associative polyacrylamide
Comprehensive properties
Polymer flooding
Harsh reservoir conditions

ABSTRACT

This work fabricated a novel star-like hydrophobically associative polyacrylamide called SHPAM used in enhanced oil recovery (EOR) processes in harsh reservoir conditions. SHPAM composed of a core of nano-silica and a layer of amphiphilic-polymeric chains was synthesized via a facile water free radical polymerization. It was systematically characterized using TEM, SEM, IR, ^{1}H NMR and DLS. Measurements from solubility, thickening efficiency, long-term stability and rheological performance indicated that the three-dimensional microstructure and intermolecular associations provided SHPAM solution with fantastically comprehensive properties, outperforming hydrophobically associative polyacrylamide. The evidence from rectangle cores in a serial model experiments implied that SHPAM was well compatible with permeable cores and it had desirable injectivity with sustainable mobility control in porous media. Moreover, core flooding tests revealed that after extensive water flooding, SHPAM with the concentration of 1500 mg/L increased the oil recovery factor by 20% in sandstone cores. This study showed the robust potential of SHPAM as a polymer flooding candidate in high temperature and high salinity reservoirs where harsh conditions associated with lack of fresh water constrain the applications of conventional polymers.

Abbreviations

^{1}H NMR	nuclear magnetic resonance spectroscopy
AA	acrylic acid
AIBA	2, 2′-azobis (2-amidinopropane) dihydrochloride
AM	acrylamide
APTES	3-aminopropyltriethoxysilane
DLS	dynamic laser light scattering
DMSO	dimethylsulfoxide
EDA	ethylenediamine
EOR	enhanced oil recovery
FNPs	functionalized PAMAM-anchored NPs
G2.0	generation two
HAPAM	hydrophobically associative polyacrylamide
HPAM	partially hydrolyzed polyacrylamide
IR	infrared spectroscopy
MA	methyl acrylate
MAH	maleic anhydride
$MeDiC_8AM$	2-methyl-*N*, *N*-dioctyl-acrylamide
NPs	nano-silica particles
PAMAM	hyperbranched polyamidoamine
SDS	sodium dodecyl sulfonate
SEM	scanning electron microscopy
SHPAM	star-like hydrophobically associative polyacrylamide
TEM	transmission electronic microscopy
TEOS	tetraethoxysilane

1. Introduction

Only a small fraction of original oil in place (OOIP) is extracted from subterranean formations by natural depletion. For the majority of conventional oil reservoirs worldwide, water is injected from the wells to displace residual oil after the initial exploitation, which is named water flooding. Nevertheless, nearly 70% of the OOIP is still trapped in geological formations even the extensive water flooding was implemented because the unfavorable mobility of water over crude oil in reservoir conditions results in water directly bypassing oil [1–3]. Therefore, it is necessary to have enhanced oil recovery (EOR) processes. Numerous laboratory studies and field applications have indicated that polymer-based process is a fairly effective EOR technique, because it fulfills three unique mechanisms: mobility ratio control [4], selectively reducing perme-

* Corresponding author at: State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, People's Republic of China.
** Corresponding author.
E-mail addresses: breakthroughliu@163.com (R. Liu), pwf58@163.com (W. Pu).

http://dx.doi.org/10.1016/j.jtice.2017.08.043
1876-1070/

Nomenclature

$[\eta]$	intrinsic viscosity number (mL/g)
c	mass concentration (mg/L)
c^*	critical overlapping concentration (mg/L)
CAC	critical associative concentration (mg/L)
E_t	cumulative oil recovery (%)
E_w	initial water flooding oil recovery (%)
f_r	resistance factor, dimensionless
f_{rr}	residual resistance factor, dimensionless
G'	storage moduli (Pa)
G''	loss moduli (Pa)
G_0	plateau storage moduli (Pa)
G_c	crossed moduli (Pa)
k	permeability (mD)
M_w	molecular weight (g/mol)
N_A	Avogadro number, 6.02×10^{23}
OOIP	original oil in place (t)
R_g	gyration radius (nm)
S_{io}	initial oil saturation (%)
t	flow time of polymer solutions or brine (s)
ΔP	pressure differential (MPa)
η_0	zero shear viscosity (Pa·s)
η_r	relative viscosity, dimensionless
η_{sp}	specific viscosity, dimensionless
λ	relaxation time (s)
ϕ	porosity (%)
ω	angular frequency (rad/s)

ability of water channels [5], and viscoelastic flow in porous media [6].

One of the most commercial water-soluble polymers used in polymer flooding process is partially hydrolyzed polyacrylamide (HPAM). HPAM consists of a large proportion of intermediate hydrophilic amide groups and the remaining of superior hydrophilic carboxyl groups [7]. Both amide groups and carboxyl groups are linearly introduced onto the backbone of polymeric chains, providing HPAM with favorable solubility and desirable viscosification in fresh water and low salinity formation water. Most recently, oilfield applications have seen polymer flooding move into new fields where everlasting properties and high cost performance in harsh reservoir conditions are paramount requirements [8,9]. However, the very limited thickening efficiency and poor long term-stability of HPAM in hash reservoir conditions hinder its wider application. It is due to the extreme deformation of the linear flexible chains at elevated temperature as well as the shielding electrostatic repulsion of carboxyl groups in the presence of high strength cations.

The literature information shows that hydrophobically associative polyacrylamide (HAPAM) in which HPAM is modified by introducing a small proportion of hydrophobic pendants onto the backbone can somehow improve the stability of polymeric chains [10–14]. Above the critical associative concentration (*CAC*), intermolecular associations between neighboring polymeric chains construct a dynamic physical network, bestowing HAPAM versatile applications [15,16]. However, pilot tests have indicated that HAPAM takes much more time to dissolve completely in water than HPAM at the equivalent concentration [6,17]. On the other hand, a "minority of polymeric species" caused by the strong intermolecular associations of hydrophobic pendants may impair the injectivity of HAPAM in porous media [18,19]. Therefore, both the nature and the component of hydrophobic moieties of HAPAM need to be deliberately designed to meet its solubility and injectivity.

In a previous study, we have initiated polymeric chains hybrid nano-silica particles (NPs) as EOR chemicals because their structures were similar to three-dimensional spheres [20]. Such water soluble star-like polymers can be engineered to controllable properties via manipulating NPs size and polymeric monomers in combination. They may expand the application of polymer flooding, especially, in hostile reservoirs where fresh water resource is usually insufficient and polymer flooding systems directly prepared with formation water are thus urgently demanded. In addition, crucial work on comprehensive properties of polymer flooding systems including viscosification, rheology, viscoelasticity, long-term stability, injectivity and oil recovery efficiency at reservoir scale is indispensable because the geological formation, temperature and salinity vary from a reservoir to another.

This study aimed to offer a novel star-like associative polyacrylamide (SHPAM) consisting of nano-silica as the core and a layer of amphiphilic polymeric-chains as the shell for polymer flooding in harsh reservoir conditions. Firstly, functionalized generation two hyperbranched polyamidoamine (G2.0 PAMAM)-anchored NPs (FNPs) were synthesized. Meanwhile, a novel hydrophobic monomer named 2-methyl-*N*,*N*-dioctyl-acrylamide ($MeDiC_8AM$) was self-prepared. Secondly, on the basis of FNPs and $MeDiC_8AM$, SHPAM was synthesized via a mild water free radical polymerization. Thirdly, SHPAM was characterized by combining transmission electronic microscopy (TEM), scanning electron microscopy (SEM), infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (^{1}H NMR) and wide angle dynamic laser light scattering (DLS). Finally, the mechanisms contributed to the comprehensive properties of SHPAM were investigated by implementing static analysis, rheological measurement and core displacement experiments.

2. Experimental sections

2.1. Materials

Tetraethoxysilane (TEOS, 99.0%), 3-aminopropyltriethoxysilane (APTES, 99.0%), Di-N-octylamine (97.0%) and methacryloyl chloride (98.0%) were purchased from Aldrich. Absolute ethanol (>99.0%), concentrated ammonia (35.0%) in water, dimethylsulfoxide (DMSO, >99.0%) and methyl acrylate (MA, >98.0%), ethylenediamine (EDA, >97.0%), maleic anhydride (MAH, >97.0%), acrylic acid (AA, 98.0%) and sodium dodecyl sulfonate (SDS, 98%) were purchased from Chengdu Kelong Chemical Reagent Co., Ltd (China). 2, 2′-azobis (2-amidinopropane) dihydrochloride (AIBA, >97.0%) were purchased from Alfa-Aesar. These chemicals were used as received. Acrylamide (AM, 95.0%) was purchased from Chengdu KeLong Chemical Reagent Co., Ltd, which was recrystallized prior to use. HPAM was purchased from SNF Floerger Group (France) with molecular weight (M_w) of 1.86×107 g/mol and hydrolysis degree of 30.3%. All the supplementary solvents and chemical reagents were of reagent grade, which were purchased from Aladdin and used without purification. Millipore distilled water with an electrical resistance of 18.0 MΩ was used. Crude oil and formation water were obtained from a certain block in Karamy Oilfield (China). The viscosity and density of crude oil at the reservoir temperature of 82.3 °C were 5.13 mPa·s and 0.852 g/cm, respectively. The SARA fractions of the crude oil were as follows: saturated hydrocarbon 73.13%, aromatic hydrocarbon 16.34%, resin 10.03% and asphaltene 0.5%. The paraffin content was around 8.3%. The natural formation water was not directly used because it contains a small amount of undissolved particles, such as clay and physical impurities. Therefore, the formation water used in this study was synthetic brine whose total salinity and inorganic composition were consistent with the natural formation water. The total salinity of formation water was 39,931.6 mg/L and the inorganic composition was $K^+ + Na^+ = 12{,}152.2$ mg/L, $Ca^{2+} + Mg^{2+} = 203.6$ mg/L, $Cl^- + HCO_3^- = 12{,}835.9$ mg/L, $CO_3^{2-} + SO_4^{2-} = 14{,}739.9$ mg/L. Cores

Please cite this article as: R. Liu et al., Star-like hydrophobically associative polyacrylamide for enhanced oil recovery: Comprehensive properties in harsh reservoir conditions, Journal of the Taiwan Institute of Chemical Engineers (2017), http://dx.doi.org/10.1016/j.jtice.2017.08.043