Star Polymer for Filtration Control in Water-based Fluids

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Abstract

In high-performance water-based drilling fluids, filtration control is a closely monitored mud characteristic. Several problems have been found that are linked to excessive invasion of aqueous filtrate into a permeable formation. A high filtrate loss often causes thick filter cake formation that lead to tight spots in the hole. Elevated temperatures and fluid loss in deep holes can cause situations such as differential sticking of pipes. At the same time, loss of filtration control catastrophically affects the rheology of the water-based fluid via excessive thickening. Seepage of the filtrate into sensitive shale formations may lead to swelling, sloughing or even cave-in. Filtrate invasion into a production zone can lead to a condition known as water blocking, where the reservoir pressure is not strong enough to drive the aqueous filtrate out of the

pores, leading to drastic reduction of oil and gas flow. In this contribution, we explore the synthesis of a novel star block copolymer fluid loss control additive using reversible addition-fragmentation chain transfer (RAFT) polymerization using arm-first approach. The star polymer developed in this work is able to provide superior filtration control performance (3 to 6 times better performance) over commercial additives. In addition, the thermal and mechanical stability of this novel material afforded direct incorporation into drilling mud formulations commonly used in the middle east drilling operations, which led to excellent fluid loss control both at room temperature and high temperature, high pressure conditions with thin filter cakes.
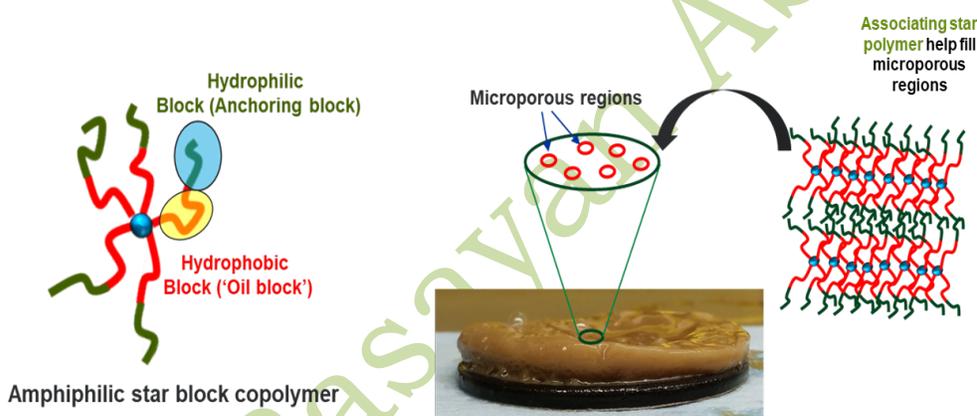
Keywords: Fluid loss control additive, star polymer, block copolymer, Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization, water-based muds

1. Introduction

Performance of a drilling fluid is determined by the physical and chemical properties of the mud such as viscosity, gel strength, mud density, and filtration (or fluid loss) control properties.[1] A good drilling fluid should have satisfactory fluid loss value and be able to deposit a thin, low permeability filter cake on the wall of the borehole for consolidation of the formation and prevention of fluid passage into the formation. Fluid loss from the mud into the formation takes place when the permeability of the wellbore rock formation allows passage of fluid into the pore space. An initial mud spurt can take place if the initial pore sizes on the formation is large. Further loss of fluid leads to the build-up of

mud solids (wall-cake) on the wall of the wellbore. A filter cake is composed of mud solids made up of native solids found in the wellbore in combination with the solids content found in the drilling mud. Filtration control of water-based fluid systems is necessary to prevent drilling problems such as excessive torque and drag, differential pressure sticking, borehole instability and formation damage.[2, 3]

Fluid loss control additives, also known as filtrate-reducing agents, are part of a group of mud additives that are designed to lower the volume of filtrate that passes through a filter medium. Commonly, HPHT filtrate loss of less than 20 mL are specified for deep, hot wells.[2] Drilling and completion fluids, fracturing fluids, and cement slurries often suffer from fluid losses upon encountering porous formation. The extent of fluid loss depends on the porosity and permeability of the

formation, and therefore, extensive fluid loss can be an expensive expenditure due to the high cost of fluids used in drilling operations. There are currently several different categories of fluid loss control additives for water-based drilling fluids that are reported in the literature and sold commercially for oil and gas drilling operations. The different fluid loss control additives studied and applied in drilling operations so far can be categorized into three different categories: (i) natural clays, (ii) natural polymers, and (iii) synthetic polymers.

The first category of fluid loss control additive is based on natural clays. Bentonite is one of the commonly used clay in the drilling operations with water-based fluids.[4] Bentonite serves a dual role in water-based muds where it increases viscosity in freshwater and seawater muds and reduces fluid loss. Bentonite hydrates more than other types of clays and is best suited to generating viscosity, developing gels for suspension, and providing filtration control. However, the performance of bentonite is greatly reduced in salty (>5000 mg/L Cl) or hard (>240 mg/L Ca) waters due to decreased hydration. In addition, bentonite clays often cause temperature induced gelation at temperatures above $120^{\circ}C$ which will then require reconditioning of the bentonite-based fluid that is pumped back to the surface or completely discarding hundreds of barrels of this fluid.[5]

To supplement the clay-based fluid loss control additives, a second category of fluid loss control additive based on natural polymer is often used. Natural polymers (biopolymers) such as cellulose, starch and lignite are abundantly available, cost effective alternative as they can be used in their natural form. However, these materials alone are not able to withstand high temperatures encountered during drilling operations. In addition, chemical degradation of natural polymers is often accelerated under alkaline conditions. Often, functionalization of natural polymers afford synthetically modified natural polymers, such as carboxymethyl cellulose (CMC), hydroxyethylcellulose (HEC), polyanionic cellulose (PAC), and metal lignosulfonates that provide improved water solubility, salt tolerance, and temperature stability.[4] However, natural polymers and their derivatives are thermally degraded (>120°C) by oxidation and hydrolysis reactions that generate low molecular weight byproducts with loss of viscosity and filtration-control effectiveness.[6] In addition, at high temperature metal lignosulfonates may lead to deterioration of rheological properties of drilling fluids due to excessive crosslinking which can be difficult to control.[7, 8]

To overcome the shortcomings of natural polymers and their modified counterparts, purely synthetic polymers based on polyacrylamides, polyacrylates, and synthetic latex particles are often used as the fluid loss control additives for water-based muds. The use of thermally stable polyacrylates and polyacrylamides as synthetic fluid loss control additives in drilling fluids was first introduced by Union Oil Corporation.[3] These synthetic polymers provide opportunities for chemical fine-tuning to accommodate the functions needed by the end user that may include variable molecular weights and different degrees of hydrolysis. Several products based on polyacrylates and polyacrylamides with average molecular weights of 0.1-3 million g/mol have been successfully deployed at temperatures exceeding 200°C. However, these products have shown to have limited sensitivity to divalent cations such as Ca^{2+}. Introduction of 2-Acrylamido-2-methylpropane sulfonic acid (AMPS)-based fluid loss control additives provided calcium and magnesium tolerance of up to 15 000 – 75 000 ppm as sulfonates are not easily chelated to divalent salts in comparison to their carboxyl group counterparts. However, most AMPS based polymers have average molecular weights of 400 000 to several million Daltons, and therefore, result in high viscosity fluids in freshwater or low salt systems.[3]

The most efficient method of controlling fluid loss is by controlling the permeability of the filter cake. Permeability of the filter cake can be manipulated by the size, shape, and deformability of fluid loss control additives under pressure.[1] Small particles with colloidal sizes of less than 2 micron provide majority of fluid loss control. Nevertheless, optimum control is achieved by having particles with different sizes. The smaller particles can wedge between larger particles to form low-permeability filter cakes. Although natural clays, natural polymers, and synthetic polymers are able to impart fluid loss control by affording filter cake with low permeability, all three additives impart high viscosities when used in water-based drilling fluid. The high viscosities can lead to pumpability issues and unwanted rheological effects such as high plastic viscosities which can reduce the ability of the drilling fluid to aid in rapid drilling. In addition, fluid loss control additives based on natural and synthetic linear polymer chains often are unable to provide resistance to mechanical and shear degradation.

In this study, we overcome these issues through the development of a novel fluid loss control additive that is based on a core crosslinked star (CCS) polymer architecture. Star polymers are part of a broad class of branched macromolecular architecture with linear arms projecting from a central branching point often called the 'core'.[9, 10] Development of reversible deactivation radical polymerization (RDRP) techniques have revolutionized the synthesis of complex polymeric architectures particularly star polymers.[9, 11-18] RDRP techniques provide several different methods to synthesize star polymers which include core-first, arm-first, and grafting-onto approaches. In this work we develop a novel star block copolymer fluid loss control additive using reversible addition-fragmentation chain transfer (RAFT) polymerization using arm-first approach.[19-27] This work highlights the first industrial application of star polymer in oil and gas exploration as fluid loss control additive in water-based drilling fluids. The star polymer developed provides superior filtration control performance (3 to 6 times better performance) over commercial additives. The superior filtration control provided by the star polymer can be attributed to the design of this material which has two important features – (i) functional block copolymer and (ii) compact structure with space-filling capacity. The core-crosslinked nature of the star polymer afforded better mechanical and thermal stability over commercial materials.

Consequently, implementing this star polymer fluid loss control additive into drilling mud formulations commonly used in the middle east drilling operations resulted in excellent fluid loss control both at room temperature and high temperature, high pressure conditions. An important rheological feature of this novel star polymer is that the addition of this material into the drilling formulations did not lead to an increase in the fluid viscosity.

2. Experimental

2.1 Material.

Acrylic acid (AA) (≥ 99%), lauryl acrylate (LA) (≥ 99%), and diethyl ether (≥ 98%) were purchased from BeanTown Chemical. Monomers were used as received with no purification or inhibitor removal. 2,2′-Azobis(2-methylpropionitrile) (AIBN) (98%), methylene bisacrylamide (MBA) (99%), toluene (≥ 99.5%), and isopropanol (≥ 99.5%) were purchased from Sigma-Aldrich. Benzoyl peroxide (BPO) (97%) was purchased from Alfa Aesar. Tetrahydrofuran (99%, stabilized with BHT) and sodium hydroxide purchased from VWR Chemicals. 2-(Butylthiocarbonothioylthio)propanoic acid (BTPA) (95%) was purchased from Boron Molecular. Potato Starch, carboxymethyl starch, hydroxypropyl starch, carboxymethyl cellulose, and polyanionic cellulose, TrueCarb 5 and TrueCarb 25 were provided by NewPark. Poly(vinyl sulfonate-vinyl amide) polymers were provided by Clariant. Partially hydrolyzed polyacrylamide and barite were provided by M-I Swaco. Xanthan gum was provided by CP Kelco. Defoamer 7500L was provided by Fritz Industries. Bentonite was provided by Wyo-Ben Inc.

2.2 Synthesis of polyacrylic acid (PAA) (Step 1).

A reaction stock solution consisting of THF (36.5 mL), acrylic acid (10.92 mL, 159.31 mmol, 11.48 g), AIBN (0.272 mmol, 44.68 mg) and BTPA (1.874 mmol, 455.5 mg, MW = 238.39 g/mol) was prepared in 100 mL round bottomed flask with a stir bar ([AA]:[BTPA]:[AIBN] = 85:1:0.1). The vial was then sealed with a septum before being sparged under nitrogen for 20 min. The mixture was heated at 60°C in a thermal bath under constant magnetic stirring for 3 h. The reaction was then stopped and cooled to room temperature. Aliquots of the final mixture was analyzed with 500 MHz ^{1}H NMR in DSMO-d$_6$ which revealed 81% monomer conversion (PAA$_{69}$) and $M_{n,theo}$ = 5210 g/mol, and aqueous SEC-MALS analysis revealing $M_{n,exp}$ = 11 700 g/mol, M_w/M_n = 1.24 (based on poly(ethylene oxide/ethylene glycol) standards, and $M_{n,MALS}$ = 11 230 g/mol, M_w/M_n = 1.01 (based on Wyatt DAWN detector). In addition, end-group fidelity was determined using the following equation: $f^{end-group} = (I^{0.9\,ppm}/3)/I^{4.7\,ppm} \times 100$, where $I^{0.9\,ppm}$ and $I^{4.7\,ppm}$ correspond to the integration values of signals at 4.7 and 0.9 ppm respectively, the end-group fidelity was determined to be close to 67%.

2.3 Synthesis of block copolymer of polyacrylic acid-*block*-poly(lauryl acrylate-*co*-acrylic acid) (PAA-*block*-(PLA-co-PAA)) (Step 2).

The PAA macro-CTA (0.83 mmol, 9.32 g) synthesized above was used in the block copolymer synthesis with no purification. Therefore, unreacted acrylic acid monomers (2.61 g) remain in the reaction mixture and continued to add onto the polymer chain in this step. Additional reagents including lauryl acrylate (5.1 mL, 18.74 mmol, 4.505 g), AIBN (0.187 mmol, 30.77 mg) and THF (23.5 mL) were added to the reaction mixture in the 100 mL round bottomed flask ([AA]:[LA]:[PAA macro-CTA]:[AIBN] = 44:23:1:0.23). The mixture was stirred for 15-30 min to homogenize the solution before sealing the flask with a septum. The reaction mixture was sparged under nitrogen for 20 min. The reaction was carried out for 18 h at 60°C in a thermal bath while stirring. The reaction was then stopped and cooled to room temperature. Aliquots of the final mixture was analyzed with 500 MHz ^{1}H NMR. Due to the difficulties in separating vinyl peaks of acrylic acid and lauryl acrylate (5.8-6.4 ppm), both monomers were assumed to have reacted equally in the reaction with an average conversion for both monomers determined to be 90%. Therefore, the block copolymer (PAA$_{69}$-b-(PAA$_{40}$-co-PLA$_{21}$)) was determined to have $M_{n,theo}$ = 19 200 g/mol, and aqueous SEC-MALS analysis revealing $M_{n,exp}$ = 67 300 g/mol, M_w/M_n = 1.16 (based on poly(ethylene oxide/ethylene glycol) standards, and $M_{n,MALS}$ = 50 640 g/mol, M_w/M_n = 1.40 (based on Wyatt DAWN detector).

2.4 Synthesis of star polymer using PAA-*block*-(PLA-*co*-PAA) (Step 3).

The PAA-*block*-(PLA-*co*-PAA) block copolymer (0.3244 mmol, 16.43 g) synthesized above was used in the star polymer synthesis with no purification. The block copolymer in THF was transferred to a 250 mL round bottomed flask followed by addition of reagents including methylene bisacrylamide (18.74 mmol, 2.89 g), AIBN (0.187 mmol, 30.77 mg) and THF (117.1 mL). The mixture was stirred for 15 min before sealing the flask with a septum. The reaction mixture was sparged under nitrogen for 30 min. The reaction was carried out for 3 h at 60°C in a thermal bath while stirring. The reaction was then stopped and cooled to room temperature. The star polymer was determined to have $M_{n,exp}$ = 81 400 g/mol, M_w/M_n = 1.15 (based on poly(ethylene oxide/ethylene glycol) standards, and $M_{n,MALS}$ = 1.727 x 10^6 g/mol, M_w/M_n = 1.31 (based on Wyatt DAWN detector).

2.5 Purification of star polymer (Step 4).

THF was removed from the final reaction mixture to yield a final yellow solid material with a strong garlic odor. The strong odor was due to the presence of trithiocarbonate functionality, which was removed in a synthetic step modified from the literature.[28] In a 250 mL round bottomed flask, 5 g (3.8 µmol) of star polymer was measured out and added with benzoyl peroxide (1.94 mmol, 0.47g), toluene (30 mL) and isopropanol (30 mL). The mixture was stirred until a homogenous mixture was seen. The flask was then sealed and purged with nitrogen for 30 min. The reaction was carried

out at 100°C for 2 h. The final mixture was then cooled with the solvent removed. The product was then redissolved in 20-30 mL of THF before drop-by-drop addition into cold diethyl ether under vigorous stirring to afford polymer precipitation. The precipitated polymer was separated from the solvent and dried in a vacuum oven at 50 °C. The desulphurized star polymer was determined to have $M_{n,exp}$ = 100 620 g/mol, M_w/M_n = 1.73 (based on poly(ethylene oxide/ethylene glycol) standards, and $M_{n,MALS}$ = 1.753 x 10^7 g/mol, M_w/M_n = 2.5 (based on Wyatt DAWN detector).

2.6 Characterization of polymers.

2.6.1 Aqueous Size Exclusion Chromatography with Multi Angle Light Scattering (SEC-MALS). Measurements were performed in a filtered buffer consisting of 0.05 M sodium bicarbonate ($NaHCO_3$), 0.1 M sodium nitrate ($NaNO_3$), and 0.02 M triethylamine (TEA) with pH 9.656. The SEC system consists of Shimadzu modular system with a DGU-20A5R degassing unit, LC20AD LC pump, CBM-20A communications bus module, SPD-20A UV/Vis detector, RID-20A refractive index detector, and CTO-20A column oven equipped with OHpak LB-G 6B guard column (dimensions: 6.0 mm ID x 50 mm) and OHpak LB-806M (dimensions: 8.0 mm ID x 300 mm L, target MW range: 500 − 20,000,000 (estimated maximum) Daltons in pullulan) purchased from Showa Denko America Inc. The MALS consists of a DAWN detector 18 angles of detection providing molar mass detection range of 200 Da- 1 GDa and molecular size range of 10-500 nm. Normalization, alignment (interdetector delay), and band broadening correction for the DAWN detector was carried out using P-50 Shodex STD P-Series pullulan which is part of Shodex Standard P-82 standard kit using the Astra software (Astra Version 7.3.2.21). The differential viscometer consists of a ViscoStar detector. The column calibration is performed based on narrow molecular weight distribution of poly(ethylene oxide)/ glycol with molecular weights of 106−1 608 000 mol^{-1} purchased from Agilent Technologies. Molecular weight analysis was carried out with the Astra software (Astra Version 7.3.2.21). Absolute weight-average molecular weights ($M_{w,SEC-MALS}$), absolute number-average molecular weights ($M_{n,SEC-MALS}$), and polydispersity index (M_w/M_n) were determined by assuming 100% mass recovery for all synthesized samples.

2.6.2 Nuclear Magnetic Resonance (^{1}H NMR). Measurements were carried out with Bruker Ultrashield 500 MHz operating at 500 MHz for ^{1}H using DMSO-d_6 as the solvent. Tetramethylsilane (TMS) was used as a reference with chemical shift (δ) of sample measured in ppm downfield from TMS.

2.6.3 Dynamic Light Scattering (DLS). Measurements were performed using a Particle Analyzer Litesizer 500 running Kalliope software (40mW, semiconductor laser, λ = 658 nm). The temperature was stabilized to ±0.1 °C of the set temperature 25°C. All samples were prepared in Milli-Q water with pH adjusted with sodium hydroxide at a concentration of ~1 mg mL^{-1} and filtered through a 0.45 µm pore size filter to remove dust prior to measurement. Hydrodynamic radii are calculated by the non-negative least squares (NNLS)

algorithm and the zeta potential was determined by the Smoluchowski approximation using the Kalliope software.

2.7 Performance evaluation of star polymer.

2.7.1 Mud Preparation and Aging Test. Formulations were mixed as provided in the Supporting Information (SI), 'Mixing Procedure for Spud Mud, Weighted Mud and Monovalent Brine Fluids', using Fann Five-Spindle Multi-Mixer® Model 9B with No. 9B29X impeller blades and rolled in Fann Roller Oven Model 705ES at the desired temperatures in Fann High Temperature Aging Cell pressurized at 500 Psi.

2.7.2 Viscometry. Rheological studies at 50°C (ambient pressure) on different water-based fluids were carried out using Fann Model 35 viscometer equipped with factory installed R1 Rotor Sleeve, B1 Bob, F1 Torsion Spring, and a stainless-steel sample cup for testing according to American Petroleum Institute Specification RP 13B. Rheological analysis with the experimental data was carried out as provided in the SI, 'Rheological Analysis'.

2.7.3 Filtration Loss Measurement with Filter Press. API filtrate loss is measured with Fann Multiple Unit Filter Press with working pressure of 100 psig at ambient temperature, and the filtering area is 7.1-in^2. Fann High-Pressure, High-Temperature Filter Press is used to evaluate the filtration at 105°C at 500 Psi. Measurements are carried out as specified in the American Petroleum Institute, *API Recommended Practice 13B-1 and 13B-2*.

3. Result and discussion:

3.1 Multistep Synthesis and Characterization of Star Polymer as Filtration Control Additive

As time and material costs were important considerations especially for future material scale-ups in preparation for field trials, the synthetic steps described herein were carried out by using raw materials such as monomers from suppliers without inhibitor removal. In addition, any side-products such as dead chains and unreacted monomers were carried forward from one step to the next, and no material purification was introduced between steps until the final desired material was made. The star polymer synthesis was carried out in four steps as described in Scheme 1. In the first step, polyacrylic acid macromolecular chain transfer agent (PAA-macroCTA) was synthesized by using reversible addition-fragmentation chain transfer (RAFT) polymerization technique. This led to 81% monomer conversion in 3 h based on ^{1}H NMR analysis as shown in SI, Figure S1 with 67% RAFT end group fidelity. SEC-MALS analysis demonstrated the correlation between RAFT end-group with polymer weights where both the absolute and relative molecular weights of PAA-macroCTA (PAA_{69}) revealed higher molecular weights than the theoretical molecular weight (SI, Table S1), which can be attributed to the RAFT end-group fidelity. PAA-macroCTA was then used in the second step of the synthesis without any purification. The remaining acrylic acid monomers and

additional lauryl acrylate monomers were added to the PAA-macroCTA (Figure S2).

The presence of dead polymer chains of PAA from Step 1 were seen during the chain extension reactions (SI, Figure S5) as dormant SEC-MALS polymer profiles in the lower retention times. The chains with RAFT end group underwent chain extensions in Steps 2 and 3 as subsequent increases in polymer molecular weights (SI, Table S1 and Figures S2-S3 & S5) to form PAA_{69}-b-(PAA_{40}-co-PLA_{21}) and star polymer, respectively, were indications of growing polymer chains. In step 2, the second block of the polymer chain with a higher weight fraction of hydrophobic lauryl acrylate over hydrophilic acrylic acid provided an overall hydrophobic nature to the second block. Therefore, the schematic representation of the star polymer designates the second block as completely hydrophobic for ease of discussions that follow. The star polymer generated in Step 3 was estimated to have 24 arms with hydrodynamic diameter of 234 nm (please see the section on 'Determination of number of arms in the star polymer' and Figures S6-S7 in the SI). As the presence of trithiocarbonate functionality can be an issue during field applications as it has the potential to generate H_2S gas during high temperature, high pressure downhole applications, removal of this moiety was quite necessary. Therefore, a desulphurization step was introduced in Step 4 using methods reported in the literature.[28] In Step 4, molecular weight of the star polymer increased despite no monomer was added (SI, Table S1 and Figures S4-S5 & S7-S8). This increase in molecular weight can be attributed to star-star coupling during the removal of the reactive thiocarbonylthio moiety. The star polymer in the final step was purified, dried and crushed to form a powdered material that can be easily dispersed in water (above pH 9) to generate dispersed nanoparticles as seen in the image in Scheme 1. The star polymer generated in Step 4 was estimated to have 62 arms with hydrodynamic diameter of
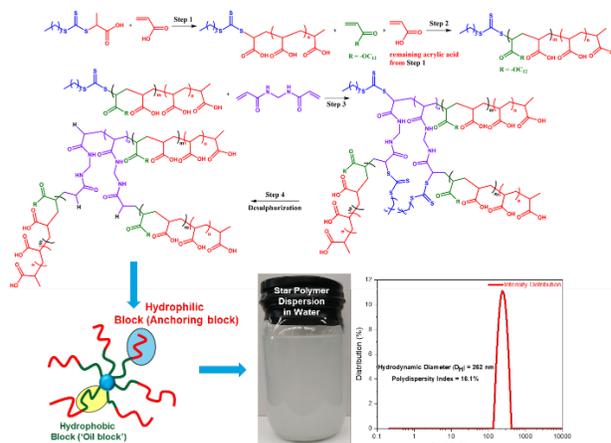
Scheme 1. Multistep synthesis of star polymer followed by dispersion in water and the resultant particle size.

262 nm with FTIR (SI, Figure S9) and TGA (SI, Figure S10) characterization carried out.

Figure 1. API filtration control performance of various additives in 4-component fluid hot rolled at 50°C for 16 h. (Note: Star* is hot rolled at 150°C for 16 h)

Table 1. Fluid loss control additives tested for filtration control performance in a 4-component fluid.

Entry	Filtration Control Additives	Filtration Loss (mL)	Thick-ness[b]
1	Control – No additive (Ctrl)	350	N.D.
2	Star polymer (Star)	7	1/32"
3	Star polymer (Star*)	6	2/32"
4	Potato starch (Starch)	19	4/32"
5	Carboxymethyl starch (CMS)	19	3/32"
6	Hydroxypropyl starch (HPS)	52	8/32"
7	Carboxymethyl cellulose (CMC)	20	1/32"
8	Short chain polyanionic cellulose (PacL)	80	6/32"
9	Long chain polyanionic cellulose (PacR)	40	1/32"
10	Poly(vinyl sulfonate-vinyl amide) I (H-1)	41	1/32"
11	Poly(vinyl sulfonate-vinyl amide) II (H-2)	70	1/32"

[b]Filter Cake Thickness (inches)

3.2 Comparing Filtration Control Performance of Star Polymer with Commercial Additives

The star polymer was designed to suit the needs of high-performance water-based mud which are often drilled under medium to highly alkaline pH (pH 9-11). To benchmark the performance of this novel additive against commercially available fluid loss control additives, a simple four component fluid system was built. The four components include water as the major fluid component, sodium hydroxide to provide alkalinity, fine calcium carbonate comprised of a mix of 15 grams of TrueCarb 5 and 15 grams of TrueCarb 25 with 30 grams total weight, and the different fluid loss control additives employed as provided in Table 1 and Figure 1. These additives were mixed in stainless-steel mixer cups, using the formulation provided in SI, Table S2, with the order of addition being water, caustic soda, fluid loss control additives and finally fine calcium carbonate with any potential
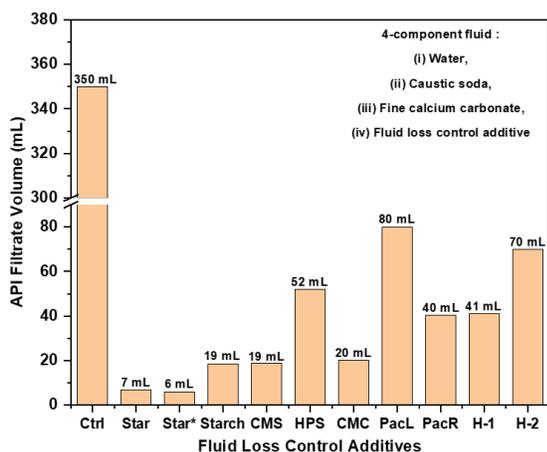
foaming issues resolved with the addition of a few drops of defoamer. The 4-component drilling fluids were then sealed in glass jars, and hot rolled at 50°C for 16 h (except for Star* which was placed in a Fann High Temperature Aging Cell pressurized at 500 Psi followed by hot rolling for 16 h at 150°C). The images of the fluids after hot rolling were captured as seen in Figure 2.

Figure 2. Appearance of 4-component fluids after hot rolling for 16 h.

API filtrate loss was then measured for 30 min with these fluids using Fann Multiple Unit Filter Press with working pressure of 100 psig at ambient temperature and filtering area of 7.1-in^2. Measurements were carried out as specified in the American Petroleum Institute, *API Recommended Practice 13B-1*. As seen in Figure 2, the micron-sized calcium carbonate alone ('Ctrl') was not able to self-suspend and hard deposition was observed. Consequently, API filtration studies in Figure 1 showed a complete fluid loss. Fluids with star polymer additives, which were Star and Star*fluids, provided transient stability to suspend the fine calcium carbonates during the time period of API filtrate loss measurements. Although the fine calcium carbonate would gradually settle over time, the star polymer was able to disperse the fine calcium carbonate and provide brief but sufficient suspension capabilities that enable fluid loss control. Furthermore, the Star and Star* fluids provided an overall better performance for filtration control (3 to 6 times better performance in reducing fluid loss values) and thinner filter cakes over commercial additives as seen in Figure 1. Starch and modified starches (CMS and HPS) also provided suspension capabilities to fine calcium carbonate. However, less efficient fluid loss control was seen for these additives when compared to fluids with star polymer additives. Synthetic and natural polymer additives such as CMC, PacL, PacR, H-1, and H-2 provided reasonable thickening to the solution to help suspend the fine calcium carbonate. However, these fluids provided subpar fluid loss control performance in comparison to Star and Star*.
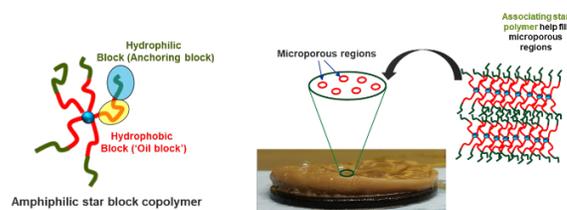
Scheme 2. Proposed fluid sealing mechanism of star polymer within the microporous regions of filter cakes.

3.2 Proposed fluid sealing mechanism of star polymer

The three categories of commercially available fluid loss control additives – natural clays, natural polymers, and synthetic polymers – are capable of providing micron scale plugging on filter cakes. Despite the differences in the chemical compositions and architectures of these fluid loss control additives, the proposed mechanism of fluid loss control often involves generation of high viscosity for tight water chelation and deposition of a highly sealed filter cake to reduce migration of water molecules. In the first mechanism, high viscosity can be generated by ionic interactions and hydrogen bonding interactions between the fluid loss control additives and water molecules. The high viscosity ensures tight chelation to water, and therefore, generating large macromolecular network that will be unable to filter through permeable formations at ease. However, with sufficiently high differential pressures in porous formations, eventually filtration takes place. Therefore, a second mechanism for filtration control during drilling is often needed. The second mechanism relies on the deposition of thin filter cakes on the porous formations to generate an impermeable layer to prevent migration of fluids into the formation. Therefore, fluid loss control additives can provide filtration control through thickening effects that help to chelate water molecules, and through generation of highly sealed impermeable layer on the formation.

Unlike the proposed mechanisms of sealing for commercial fluid loss control additives, a superior filtration control performance was achieved with the designed star polymer over commercial additives in the 4-component fluid system due to two important features: (i) functional block copolymer and (ii) space-filling capacity of the compact star polymer. It is important to highlight that fine calcium carbonate helps to reduce porosity of filter cakes but still leaves behind micron-sized porosity that promotes migration of water molecules leading to fluid loss. The compact nature of star polymer (Scheme 2) helps to fill these microporous regions through hydrophobic association. The hydrophobic association in water is made possible due to amphiphilic block copolymer nature of the star molecule where the anionic hydrophilic block acts as the anchoring block to a medium such as calcium carbonate while the hydrophobic

block avoids water molecules by creating a microviscous regions in the micron cavities of filter cakes which consequently prevent passage of water molecules.

3.3 Incorporation of star polymer in drilling fluid formulations

In this section, three field mud systems commonly used in the middle east for drilling operations were explored with the novel star polymer fluid loss control additive.[29] These drilling fluids include spud mud (bentonite based unweighted mud), gelled polymer mud (weighted mud), and low solids non-dispersed polymer mud (monovalent brine fluid) were designed to test the efficacy of the star polymer in providing filtration loss control. The preparation of these various muds can be found in the SI under the section titled 'Mixing Procedure for Spud Mud, Weighted Mud and Monovalent Brine Fluids'.

3.4.1 Spud Mud Fluids and Gelled Polymer Fluids

Spud muds are water-based drilling fluid formulations used in drilling shallow formations with large hole diameters (i.e. 36"-26"). Spud mud is often composed of flocculated bentonite that provides the necessary thickening properties to the fluids. Despite having simple compositions, spud muds provide desired rheological properties that help to carry out large gravel cuttings from shallow depths.[29] Spud mud fluids were designed in this study as provided in Table 2 for fluid loss measurements. Achieving API fluid loss control of less than 6 mL and HPHT fluid loss control of less than 20 mL with filter cake thickness of 1/32"-2/32" for both tests were determined as the criteria for success. In terms of rheology,
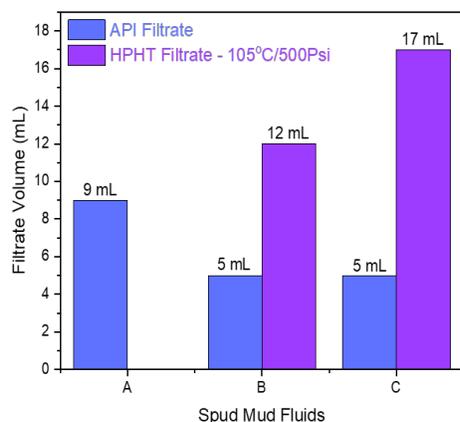

Figure 3. Filtration loss studies in three different spud mud fluids.

the lowest possible plastic viscosity (PV) and yield point (YP) of above 35 $lb_f/100ft^2$ were needed. The rheological parameters of these fluids were measured with a Model 35 viscometer and fitted to Bingham-Plastic and Herschel-Bulkley models as provided in the SI section titled 'Rheological Analysis'.

Fluid A was designed as a base fluid without a fluid loss control additive. This fluid was designed as a control fluid which provided API filtrate loss of 9 mL (Figure 3) and a filter cake thickness of 4/32" (Table 3). Further testing of fluid A for high pressure, high temperature (HPHT) filtrate loss was not carried out due to poor API filtrate performance. In fluid B, introduction of the star polymer additive led to reduction of API filtrate to 5 mL (Figure 3) and a thinner filter cake (Table 3). Further HPHT filtrate loss testing of fluid B provided low fluid loss value and slightly thicker but acceptable filter cake

Table 2. Spud mud fluids (8.7 lb/gal) with pH 9-10 designed and tested for API and HPHT filtration loss studies:

Entry	Fluid Formulations (g)	A	B	C
1	Water	330	330	330
2	Star Polymer	0	4	4
3	Caustic Soda	0.1	0.9	0.9
4	Bentonite	30	30	30
5	Xanthan gum	0.3	0.3	0.3

Fluid A (Control) – Rolled at 50°C for 16 h; fluid B – Rolled at 50°C for 16 h; and fluid C – Rolled at 105°C for 16 h.

thickness. The addition of the star polymer fluid loss control additive provided fluid with slightly lower plastic viscosity when compared to fluid A (Table 4 and SI, Table S3). Despite the drop in the YP for fluid B when compared to fluid A (Table 4), the YP value remains above the required threshold. Fluid C was designed with similar composition as fluid B, but hot rolling was carried out at 105°C for 16 h. It was highly likely that the xanthan gum was partially degraded at 105°C due to lower PV and YP observed in fluid C when compared to fluid B. Nevertheless, the high temperature stability of the star polymer provided low fluid loss values and thin filter cakes in both API and HPHT filtration tests (Figure 3 and Table 3, respectively). All three fluids provided pseudoplastic characteristics with similar consistency factor.

Table 3. Filter cake thickness of fluids A-C.

Entry	Fluids	A	B	C
1	API filter cake thickness (inches)	4/32"	1/32"	1/32"
2	HPHT filter cake thickness (inches)	-	2/32"	4/32"

Table 4. Rheology of spud mud fluids A-C measured with Fann Model 35 viscometer after hot rolling (AHR).[a]

Fluids	Bingham-Plastic Model			Herschel-Bulkley Model		
	PV (cP)	YP ($lb_f/100ft^2$)	LSYP ($lb_f/100ft^2$)	τ_o[b]	n	k
A	44.8	74.7	32.0	32.0	0.6	2.1
B	42.7	49.1	12.8	12.8	0.6	1.6
C	32.0	37.3	10.7	10.7	0.6	1.2

[a] PV – Plastic viscosity, YP – Yield point, LSYP – Low Shear Yield Point, τ_o – Zero shear yield point, n – flow behavior index and k – consistency factor. [b] T_0 in $lb_f/100ft^2$ unit.

In order to test the effectiveness of the star polymer as a fluid loss control additive in weighted muds, gelled polymer fluids were designed as provided in Table 5. The weighted

polymer mud fluids were composed of bentonite and xanthan gum to provide viscosification, partially hydrolyzed polyacrylamide (PHPA) to provide shale inhibition, barite as a weighting agent to provide the necessary density, sodium hydroxide to provide the necessary alkalinity, and fine calcium carbonate (a mix of 15 grams of TrueCarb 5 and 15 grams of TrueCarb 25) to act as bridging agent. Achieving API fluid loss control between 3-4 mL with filter cake thickness of 1/32" for both tests were determined as the criteria for success. Fluid D was designed as the base fluid and fluids E to G were variations of the base fluid with different compositions of star polymer and fine calcium. Base fluid D provided poor API fluid loss control (Figure 4 and Table 6) and fluid E with fine calcium carbonate did not improve fluid loss control despite thin filter cakes observed for both fluids. Fluid F with the star polymer provided fluid loss value that was almost half to that observed in fluid D and E, and thin filter cake. No further reduction in fluid loss value was observed in Fluid F composed of fine calcium carbonate and star polymer.

Table 5. Weighted mud fluids (13 lb/gal) with pH 9-10 designed and tested for API filtration loss studies: Fluids D to G were rolled at 50°C for 16 h.

Entry	Fluid Formulations (Amount in grams)	D	E	F	G
1	Water	287	287	287	287
2	Bentonite	3	3	3	3
3	Star Polymer	0	0	1	1
4	Sodium hydroxide	0.12	0.12	0.3	0.3
5	Xanthan gum	0.8	0.8	0.8	0.8
6	PHPA	1.3	1.3	1.3	1.3
7	Fine calcium carbonate	0	30	0	30
8	Barite	234	234	234	234

It is important to note that the addition of fine calcium carbonate did not help improve fluid loss control as bentonite in these fluids may have supplanted the role of fine calcium carbonate. In comparison to the base fluid D and fluid E, fluids with the star polymer provided very similar rheology (Table 7 and SI, Table S4) with improvements in YP values and consistency factors.

Table 6. Filter cake thickness of fluids C-F after API filtration test.

Fluids	D	E	F	G
API filter cake thickness (inches)	1/32"	2/32"	1/32"	1/32"

Table 7. Rheology of gelled polymer mud fluids D-G measured with Fann 35 after hot rolling (AHR) at 50°C for 16 h.

Fluids	Bingham-Plastic Model			Herschel-Bulkley Model		
	PV (cP)	YP (lb$_f$/100ft^2)	LSYP (lb$_f$/100ft^2)	τ_o[a]	n	k
D	18.1	46.9	11.7	11.7	0.4	3.8
E	21.3	53.4	13.9	13.9	0.4	4.1
F	16.0	54.4	8.5	8.5	0.3	7.8
G	17.1	61.9	10.7	10.7	0.3	9.2

[a] τ_o in (lb$_f$/100ft^2)

3.4.2 Low solids non-dispersed polymer fluids

Salt-polymer muds are often used for shale stabilization and avoiding sloughing and hole enlargement due to dissolution of hard salt formations that are often composed of sodium, magnesium, or potassium chlorides. Salt polymer
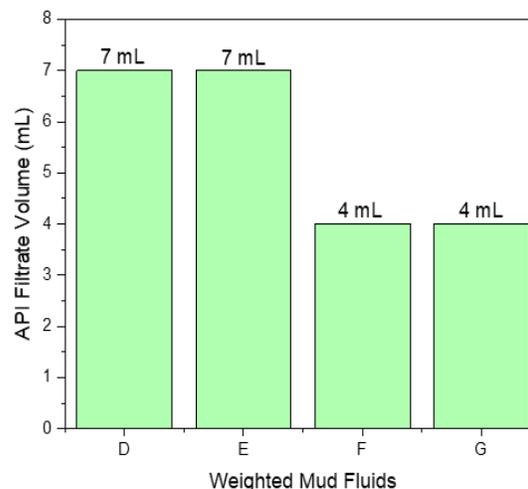

Figure 4. API filtration loss studies studied in four different weighted fluids.

muds used in this study consists of low solids non-dispersed polymers.[29] Low solids non-dispersed polymer mud (monovalent brine mud) formulations were designed as provided in Table 8. Achieving API filtrate loss of 4 mL or less and HPHT (105°C) fluid loss of 20 mL or less with filter cake thickness of 1/32"-2/32" were determined to be criteria for success. Fluid H designed with no fluid loss control additive provided poor API filtrate loss value (Figure 5), and therefore, no HPHT filtration test was carried out. In the presence of the star polymer, fluid I provided 3 times reduction in API fluid loss value in comparison to fluid H. Further testing of fluid I in HPHT environment (105°C and 500 Psi) provided a fluid loss value of 15 mL. Fluid J with higher content of calcium carbonate provided similar API fluid loss value as Fluid I, but a decrease in HPHT fluid loss was observed. Fluids I and J satisfied the API and HTHP filtration and filter cake thickness (Table 9) criteria needed for low solids non-dispersed polymer mud. Rheological profiles of fluids I and J were close to base Fluid H (Table 10 and SI, Table S5). Attempts to lower the star polymer loadings from 6 grams to 4 grams, as provided in SI, Tables S6-S9 and Figure S11, resulted in slightly higher fluid loss values (API fluid loss: 5 mL and HPHT fluid loss: 15 mL). Fluid K was designed with a similar composition as Fluid J, but hot rolling at 105°C was carried out for 16 h before API and HPHT filtration tests. Fluid K provided a lower LSYP compared to fluid H-J which affected the suspension capabilities of the mud under static conditions, and consequently, higher fluid loss values and thicker filter cake deposition for API and HPHT filtrations were observed.
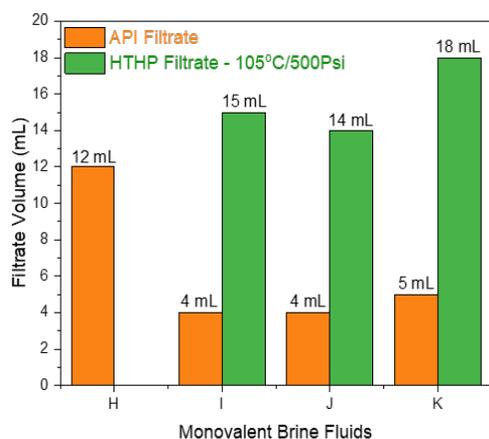
Figure 5. Filtration loss studies in four different monovalent brine fluids.

Table 8. Monovalent brine fluids (9.3 lb/gal) with pH 9-10 designed and tested for API and HTHP filtration loss studies: Fluid H (Control) – Rolled at 50°C for 16 h; Fluids I & J – Rolled at 50°C for 16 h; and Fluid K – Rolled at 105°C for 16 h.

Entry	Fluid Formulations (Amount in grams)	H	I	J	K
1	Water	324	324	320	320
2	Sodium chloride	21	21	21	21
3	Star Polymer	0	6	6	6
4	Caustic soda	0.1	1.5	1.6	1.5
5	Xanthan gum	1.5	1.5	1.7	1.7
6	Fine calcium carbonate	30	30	40	40

Table 9. Filter cake thickness of fluids H-K.

Entry	Fluids	H	I	J	K
1	API filter cake thickness (inches)	1/32"	1/32"	1/32"	1/32"
2	HPHT filter cake thickness (inches)	-	1/32"	1/32"	3/32"

4. Conclusions

In this study, a novel star block copolymer fluid loss control additive was developed, and detailed synthetic steps were provided and discussed. In comparative testing to commercial fluid loss control additives, the star polymer additive afforded 3- to 6-times better performance in reducing filtrate loss. The superior filtration control provided by the star polymer can be attributed to the design of this material which has two important features – (i) functional block copolymer and (ii) compact structure with space-filling capacity. The star polymer was also directly applied into field mud formulations commonly used in the drilling operations in the middle east. The three field muds that were designed for this testing include spud mud fluids, gelled polymer fluids, and low solids non-dispersed polymer fluids. In all three mud systems, excellent API and HTHP filtration loss control were achieved with thin filter cakes. Furthermore, the addition of star polymer additive in these mud systems led to no increase in plastic viscosities which can be detrimental for drilling operations.

6. Notes and References

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